WATER QUALITY IN THE UPPER LITTLE TENNEESSEE RIVER AND ITS POTENTIAL EFFECTS ON APPALACHIAN ELKTOE

By

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A Thesis
Submitted to the
Faculty of the Graduate School
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A thesis presented to the faculty of the Graduate School of
Western Carolina University in partial fulfillment of the
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ABSTRACT

WATER QUALITY IN THE UPPER LITTLE TENNEESSEE RIVER AND ITS POTENTIAL EFFECTS ON THE APPALACHIAN ELKTOE MUSSEL (*ALASMIDONTA RAVENELIANA)*

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Western Carolina University (August 2011)
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Mussels are an indicator species for water quality due to exposure to acute water pollutants from their filter feeding life style (Augspurger 2003). Mussels are also more susceptible to trace metal exposure than many other aquatic organisms due to their behavior of burrowing in fine grained sediments and feeding on detritus and particulate matter (Wilson 2008). Metal accumulation is proportional to the assimilation efficiency of metals from food (Wang and Fisher 1999) and through the examination of waters and sediments in which these organisms live insight into potential effects posed by harmful trace metals can be identified. Since 1993, the Appalachian elktoe (*Alasmidonta raveneliana*) has been federally listed as a critically endangered species. An area of high population density for the elktoe mussel was the Upper Little Tennessee River. In 2006 biologists began to notice a severe decline in the elktoe population during routine mussel monitoring surveys. In order to understand the water quality threats posed to elktoe mussels, water quality parameters were monitored during this project.

From January 2009 – January 2010, HACH water quality sondes were deployed at three monitoring sites along the Upper Little Tennessee River to evaluate the aquatic

habitat and determine surface water quality. Analyses of water samples and shell material for selected trace metals were conducted using an ICP-MS. Temporal variations of total suspended sediment loads during floods were also documented at these sites. Further observation into the presence of copper was accomplished through porewater sampling along the reach of the Upper Little Tennessee River known to currently contain elktoe mussel populations.

Although other studies have found trace metal concentrations of barium, chromium, nickel, lead and zinc in sediment well above probable effect thresholds, the portion of these trace metals found in bioavailable concentrations appears to be low on the basis of shell and copper data from porewater investigations. Copper levels did show wide local variability, suggesting that levels are significantly different on a localized scale. Moreover, the porewater samples were collected from September 2010 to January 2011, and therefore do not account for high inputs of common local fertilizers and/or significant changes in temperature and pH in the warmer seasons.

Copper and zinc levels in the water column rose significantly during storm events observed during this project posing a potential threat to elktoe mussels. Specific threats include elevated sediment transport rates leading to increased turbidity and enhanced trace metal loads during rainfall events. Sediments also could be reworked from upstream impoundments during high water events, such as the back to back hurricanes of 2004 after which the mussel declines were noticed. These observations are consistent with other studies that have found high concentrations of trace metals, including copper and zinc, in sediments of Lake Emory and the Little Tennessee River that locally exceed probable effect thresholds for aquatic biota. Thus, trace metal-rich sediments located at the upstream terminus of the elktoe mussel habitat appears to pose a significant threat to mussel populations.

INTRODUCTION

The Appalachian elktoe (*Alasmidonta raveneliana*) is one of only three endangered species currently listed in the Upper Little Tennessee River (the other two are the spot fin chub (*Erimonax monachus*) and pearly-winged mussel (*Pegias fabula*)). None of these species are present in the basin upstream of Porter's Dam on Lake Emory in Franklin, NC and it is likely that the stressors affecting the elktoe mussel are also playing a role in the observed declines of the spot fin chub and pearly winged mussel in the Upper Little Tennessee River basin (Figure 1). The elktoe mussel and spotfin chub comprise similar habitats and while the elktoe mussel has been on the endangered list since 1993, the spotfin chub was federally listed as threatened in 1977.

An effort to restore elktoe mussel populations began in the mid-1990s when only two populations were known to exist. After hurricanes Ivan and Francis in 2004, populations in the Little Tennessee River were greatly reduced and have steadily declined; by 2006, populations in the Little Tennessee River had decreased by 80% (Fridell 2010 personal communication). Surveys carried out by the NC Wildlife Commission in the summer of 2004, months before hurricanes Ivan and Francis impacted the basin, produced findings of over 700 elktoe mussels below the Lake Emory dam in Franklin; in 2010 repeat surveys were lucky to find 2-3 individuals for any given survey reach along this stretch. For every hour spent surveying in 2004 biologist found an average of 6.1 elktoe mussels, but by 2006 this number dropped to an alarming 0.8 mussels per hour surveyed (Fraley 2010).

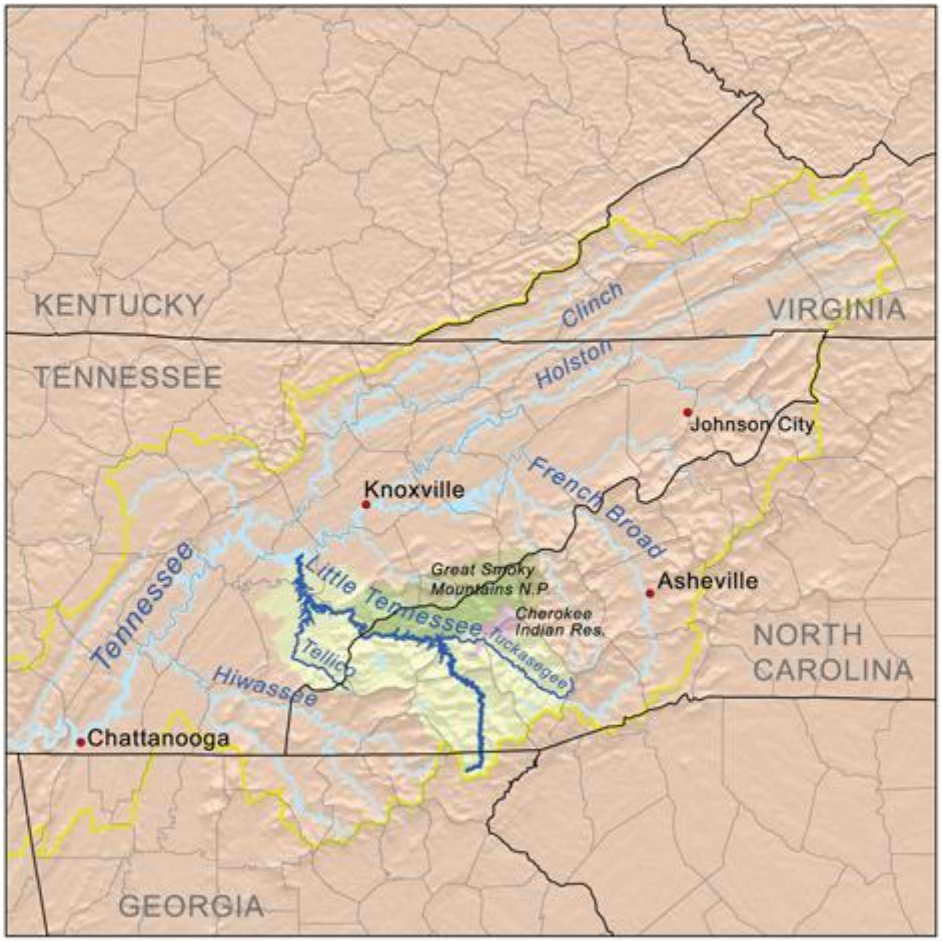

Figure 1. Little Tennessee River basin map.

One of the many hypothesized causes for this decline is a reduction in sediment and/or water quality associated with a combination of sedimentation from land use changes, agricultural runoff, mining, and trace-metal contamination. Trace metals occur naturally in the earth's crust posing the constant threat of increased contamination during large land disturbing activities such as urbanization. Many rock formations found in the Upper Little Tennessee River basin contain high concentrations of trace metal rich minerals which pose great contamination risks during land alteration practices. Trace elements entering fluvial systems are primarily sorbed to particulate matter and especially very fine sediments (Foster and Charlesworth 1996). These elements pose direct threats to native mussel populations due to their feeding behavior on fine sediments, particulate matter and detritus. Most current water-quality criteria are based on fish and macro-benthic species due to their known impacts from contamination; however, mussel species have recently been found to often be a more highly sensitive indicator species (Augspurger 2003).

Alterations in sediment and water quality, and their potential impact on biota, are examined in this study through the observation of selected water quality parameters. These parameters include dissolved and total (dissolved plus particulate) trace metal concentrations in water samples and mussel shells along with observations of temperature, specific conductivity, turbidity and dissolved oxygen to obtain an understanding of the aquatic environment to which these mussels are currently exposed.

In addition, these parameters may alter trace metal speciation (and bioaccumulation) at the study sites by defining the physio-chemical environment in which these metals are found. One concern is that over time, changes in pH, temperature or specific conductivity could lead to changes in trace metal mobility or form. No direct cause is currently known for the observed elktoe mussel declines; however, by studying the environment and surrounding threats to the existing populations on the Upper Little Tennessee River, there is a greater chance of developing a strong method for mussel reintroductions and reversing the declining trend in these populations.

Trace metals were focused on in this study due to their high historical occurrence of contamination in mussel populations (Farris and Van Hassel 2007). It is also well documented that trace metals such as copper have negative effects on mussel survivorship (Wang 2006, Newton 2006, March 2007). Furthermore, young mussels are often more sensitive to copper than many other species, including those that are commonly used to establish water quality standards (Augspurger 2003). Findings such as these have led to further investigations of water quality standards and examination of juvenile mussel response to water quality contaminants (Ward 2006; Cope 2008).

OBJECTIVES

The aim of this study was to observe and analyze water quality in the Upper Little Tennessee River in order to understand the threats posed to species which are experiencing large population declines, such as the elktoe mussel. Trace elements such as copper, chromium, lead, nickel, and zinc are known to have adverse effects on mussel populations, such as wasting of the mussel shell, inability to feed and reproduce and increased mortality on smaller juvenile mussels and glochidia (Strayer 2008).

In addition to trace metal toxicity, mussels can be affected by factors such as high temperatures, increased turbidity, changes in pH and decreases in dissolved oxygen (Dimmock and Wright 1993; Pandolfo 2010; Wang 2007). These parameters were observed over a one-year period to get an understanding of the current state of the aquatic habitat in which these mussels are living and observe any possible threats that may exist to population success.

Possible threats to aquatic health in this basin include the introduction of chemicals and trace metals from mining, industrial waste and agricultural practices. By examining water quality parameters and trace metal content across this basin an understanding of these threats and their extent can be examined. An upper and lower site on the main channel was chosen for this study, along with tributary site, Cartoogechaye Creek, which is a major tributary to the Upper Little Tennessee River and the municipal water source for the town of Franklin, NC.

Several factors may be combining to create the declines observed in mussel populations, such as trace metal contamination, temperature fluctuations outside aquatic life thresholds and/or high turbidity and sedimentation rates. With that in mind, this project tested multiple hypotheses in order to determine the effects of water quality on the Upper Little Tennessee River: (1) trace metal water and porewater contamination in the basin poses a potential threats to aquatic life, (2) thresholds of environmental water quality parameters (pH, temperature, dissolved oxygen and turbidity) extending beyond aquatic life standards, and (3) Trace metals accumulate in elktoe mussel shells over time due to the degradation of sediment and water quality across the basin.

Appalachian Elktoe Ecology

Appalachian elktoe mussels belong to the *Unionidae* family of freshwater bivalves and are a species of the *Alasmidonta* genus named *raveneliana.* These mussels inhabit sand and gravel substrate among cobbles and boulders and under flat rocks, usually in moderate current at depths of less than one meter (Parmalee and Bogen 1998). Elktoe prefer clear shallow water where they spend much of their life burrowing partially or wholly in silt and sandy sediments. During the early stages of their life cycle these mussels are transported on the gills of fish, which are targeted by adult spawning mussels with large attractive lures displayed between the bivalves. These lures are evolutionarily selected to attract the individual species' host fish. For the Appalachian elktoe this fish species has been define by Watters (1994) as being the banded sculpin (*Cottus carolinae*). It is also expected that the mottled sculpin (*Cottus bairdii*) serves as a host in NC waters due to its great abundance and similarities. Although many declines in mussel fecundity have been attributed to a reduction in host species, both of these sculpin species have been found to be increasing steadily in the Upper Little Tennessee and Tuckasegee Rivers according to routine surveys (NCDENR 1998).

Alasmidonta mussels are sensitive to alterations in habitat dynamics, with several species experiencing population declines due to dams and associated hypolimnetic discharges, sedimentation and pollutants (EPA 2008). Freshwater mussels serve well as a bio-indicator species due to their range of tolerances to toxic contaminants, often exhibiting a variety of sensitivities based on species, life stage (glochidium, juvenile, or adult) and environmental conditions. Many species of freshwater mussels are also long-lived, further increasing their value as an indicator species with relation to legacy contaminants. Most freshwater mussels are sedentary filter feeders, burrowing into sediments and exhibiting suspension and deposit feeding behaviors, making them susceptible to contamination from both the water column (dissolved or attached to suspended particles) and streambed sediments (Naimo 1995). In addition, many species are fairly large, containing ample soft tissue for chemical analysis and their spent valves leave a historical record (EPA 2008). *Alasmidonta* are valuable indicators of habitat and water quality, as they generally inhabit clear, good quality, flowing habitats with stable substrates (Watters 1995 and Bogan 2002).

During this study trace metals were focused on because of their observed concentrations above probable effect thresholds in local sediments from recent sampling (Miller 2010). Although it is well known that mussels accumulate trace metals readily, rates of accumulation can vary greatly based on mussel species, size, growth rate, and metal species (Adams 1981; Pip 1995). However, past studies have shown that higher concentrations of Cd, Cu, Pb and Zn in the annuli of bivalve shells can be linked to higher concentrations of those trace elements in the environment (Schetter and Pearce 1996, Richardson 2001, Markich 2002 and Liehr 2005). With this in mind, trace metal concentrations observed in elktoe mussel shells during this study should be compared with background concentrations of bedrock and soils, along with axial river channel and channel edge sediments recently analyzed in Miller 2010 (Table 1).

Table 1. Background trace metal concentrations of granite, shale and soil compared to analyzed local sediment, water column, porewater and shell concentrations.

Element	Granite average (µg/g)	Soils average (µg/g)	Soils range (µg/g)	River Channel average (ppm)	Channel Edge average (ppm)	Water Cloumn rane (µg/L)	Pore-water range (µg/L)	Shells range (ppm)
Copper	20	25	<1-700	134	347	<1-33	<1-8	7-42
Lead	17	19	<10-700	14	3	<1	---	2-38
Nickel	10	19	<1-700	22	27	<1-5	---	<1
Zinc	50	60	<5-2900	92	23	<1-43	---	2-81

STUDY AREA

The Upper Little Tennessee River originates in Northern Georgia and immediately crosses the North Carolina state line (Figure 2); approximately 19 kilometers north of the state line the Cullasaja River joins the Little Tennessee River in Franklin, NC before being impounded by Porter's Dam on Lake Emory. Downstream from Lake Emory the Upper Little Tennessee River flows through a rural landscape comprised of several small farms and residencies before being bordered by the Needmore Conservation Tract. The Needmore Conservation Tract encompasses both channel edges of the river for 11 kilometers before becoming impounded again by a TVA dam forming Fontana Lake. As the drainage exits Fontana Dam it continues through Chattanooga, Tennessee, flows northwest into the Ohio River and eventually drains into the Gulf of Mexico.

Geologically, the Upper Little Tennessee River lies within the Blue Ridge Mountain physiographic province. The river channel has cut down to bedrock in many areas along its course, and rock ledges are exposed for much of the Upper Little Tennessee below Porter's Dam in Franklin, NC. Areas of sediment deposition have been created by large eddies downstream of these bedrock outcrops and along stream banks. The Upper Tennessee River basin encompasses approximately 34,424 square kilometers including the entire drainage of the Little Tennessee River and its tributaries upstream of the USGS gaging station on the Tennessee River at Chattanooga, Tennessee (NCDENR 2011).

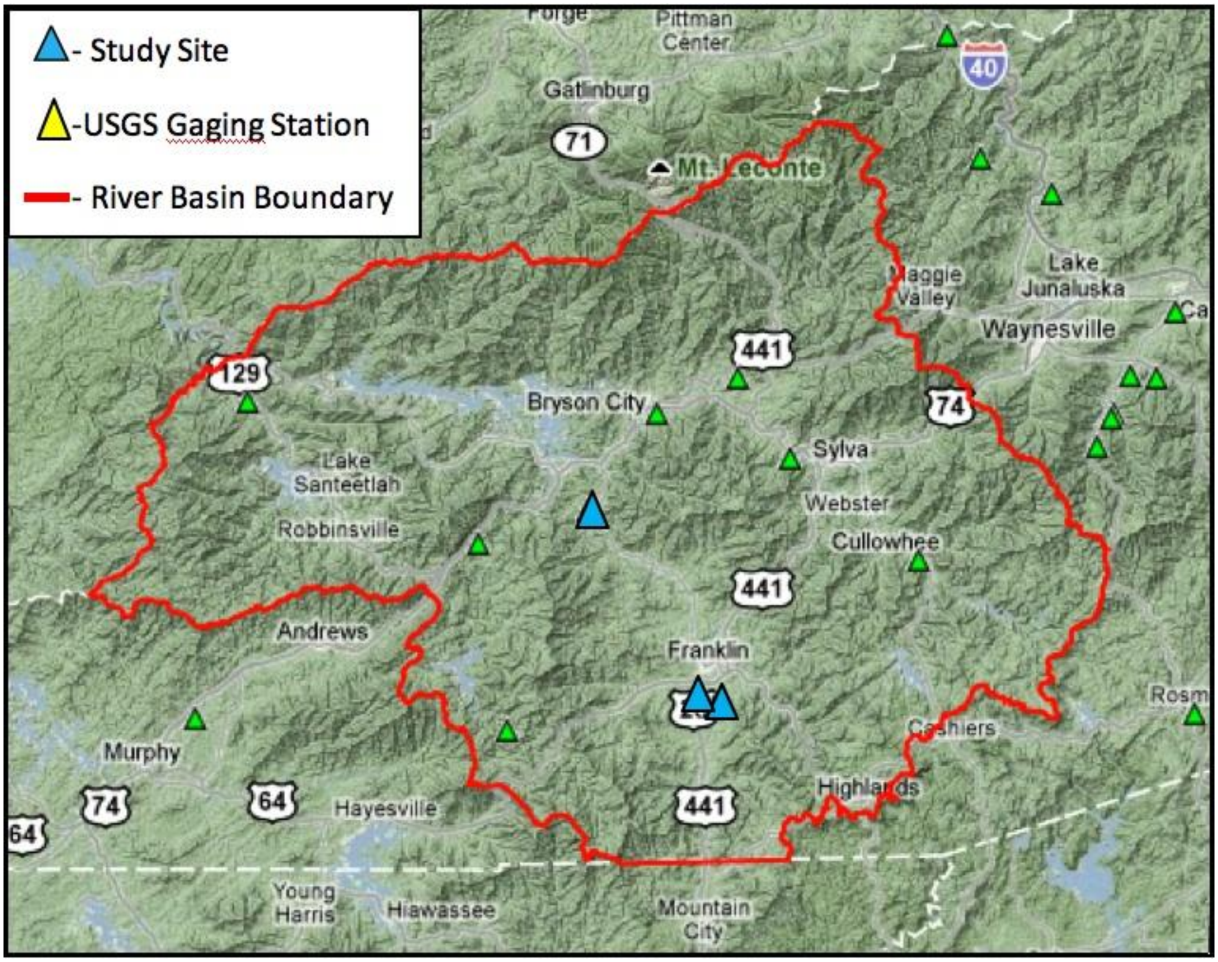

Figure 2. Location of Little Tennessee River basin in North Carolina with study sites highlighted.

The primary rock units of the Upper Little Tennessee River basin are the Nantahala, Wehutty, and Anakeesta formations and to a lesser extent the Copper Hill formation. These rocks are characterized by abundant dark gray and black graphitic and sulfidic layers (NCGS 1985). This geologic province contains Middle Proterozoic felsic gneiss derived from sedimentary and igneous rocks. The gneiss is locally migmatitic and mylonitic and variably inter-layered with amphibolites, calc-silicate granofels and rarely marble, intrusions of Late Proterozoic mafic and felsic plutonic rocks and clastic metasedimentary and metavolcanic rocks of the Ocoee Supergroup (NCGS 1985). Anakeesta, Wehutty and Copper Hill formations within these groups, include sulfide minerals such as pyrite, which during chemical weathering produces a weak sulfuric acid that can adversely affect streams by making the water more acidic (decreasing the pH). Human activity such as road construction can expose fresh sulfidic rock to the atmosphere and increase acid runoff (NCDENR 1997).

The Blue Ridge Province is a mountainous area of steep ridges, inter-mountain basins and valleys that intersect at all angles giving the area its rugged character. The Blue Ridge contains the highest mountains in eastern North America, with about 125 peaks exceeding 1524 meters in elevation. The steep slope that separates the mountains and Piedmont is the blue-ridge escarpment. Headward erosion of the Blue Ridge Mountains by Atlantic-flowing streams produces this sharp topographic break (NCGS 1985).

Forest covers more than 64% of the study area with 27% agricultural, 6% urban, 2% open water and 1% barren due to mostly to mining. The entire watershed is located in a temperate climate with temperatures and rainfall being related primarily to elevation. Temperatures decrease approximately 1.6° C for every 305 meter increase in elevation; while annual precipitation ranges from approximately 102 centimeter in some low-lying sheltered areas to more than 229 centimeter at elevations above 1830 meters.

The US Forest Service has designated three segments of the Little Tennessee, Tuckasegee, and Cheoah rivers, comprising 130 kilometers, as “critical habitat” for the elktoe mussel. The lower reaches of the Upper Little Tennessee River observed during this study are included in this designation. These lands are surrounded by the Needmore

Conservation Tract (LTLT 2011) which is 89% forested and is noted as having generally excellent water quality (NCDENR 2004).

METHODS

Contamination from trace metals was tested through storm and porewater sampling, including chromium, copper, lead, nickel and zinc analysis from the storm samples and copper analysis from the porewater samples. Mussel shells were analyzed for trace metal content in order to determine bioaccumulation through time due to the incidental incorporation of many trace metals into the shell during shell growth (Imlay 1982). Water quality parameters were collected through multi-parameter water quality probes in order to determine any environmental changes which could be leading to the declines over time. Any of these factors could combine or work alone to affect mussel survival and fecundity rates, leading to population declines such as recently observed in this watershed.

Monitoring Sites

At all sites where trace metal analyses were carried out, water quality sondes were deployed for data collection and freshly dead to moribund elktoe mussel shells were collected where present. Hach MS-5 multi-parameter sondes were used with temperature, specific conductivity, dissolved oxygen and turbidity meters attached to the same probe, creating a multi-parameter data collection platform. Collection of water quality data for a 1-year period was carried out at three USGS stream gaging stations all located in the Upper Little Tennessee River basin, including Cartoogechaye Creek in Franklin, NC, Little Tennessee River at Prentiss and Little Tennessee River at Needmore

(Figure 2). Collected parameters included temperature, specific conductivity, dissolved oxygen, turbidity, stage, discharge, trace metal content analyzed by ICP-MS from water samples collected during floods, and local precipitation data from USGS rain gages.

The above-mentioned water and sediment data were compared to collections of mussel shells from the Upper Little Tennessee and Tuckasegee Rivers analyzed for trace metal contaminant concentrations. Thus, this investigation provides observations of current trace metal contaminants contained within sediment and surface water as well as any contaminants that have accumulated in the mussel shells over their lifespan.

Temperature, specific conductivity, dissolved oxygen and turbidity data were collected using HACH water quality sondes installed at each gaging station through the cooperation of USGS, NCDENR and Coweeta Hydrologic Station (Gragson 2008). These sites were serviced and calibrated during site visits which occurred once every two weeks from January 1st 2010 – January 1st 2011. Servicing of the water quality sondes included data comparison to a field probe, ensuring that drift or siltation of the probes was corrected for and calibrating for dissolved oxygen, turbidity and specific conductivity with standard solutions. Temperature was also checked using the field probe upon each visit; however this parameter was factory calibrated and once the temperature was determined to be off, the probe was pulled, replaced and sent back to HACH for repair. Other issues with the probes which warranted replacement and repair throughout the year included failure of either of the dissolved oxygen, turbidity, or specific conductivity sensors to calibrate. Coupled with discharge measurements, these data were used to create hydrographs throughout the year for an overall view of river hydrology over the course of one year.

Analysis of chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn) in water and shell samples provided an overview of potential threats to biota from these contaminants which were then compared with current guideline values (NCDENR 1998). Trace metal analyses were carried out at the Nevada Bureau of Mines and Geology in Reno during June and July 2010. Geochemical analysis included ion chromatography and inductively coupled plasma-mass spectrometry (ICP-MS; Faires 1993; Martin 1994; Garbarino 1999) on water grab samples collected at all three gaging stations. ICP-MS analysis was also carried out on mussel shells collected for this project to determine contaminant uptake experienced by individual mussels.

Shells obtained during mussel surveys with the NC Wildlife Commission and US Fish and Wildlife Service were taken to the Nevada Bureau of Mines and Geology (NBMG) lab and analyzed using ICP-MS to determine the trace metal concentrations in individual elktoe mussels during the recent decline of this species. ICP-MS analysis involved digesting the mussel shells with trace metal grade nitric acid. Each mussel shell segment analyzed consisted of a cross section cut through the growth rings to obtain a representative sample across the mussel’s lifespan. This segment was covered with 15 ml trace metal grade nitric acid and 15 ml Hydrofluoric acid and then heated on hot plates until all shell material dissolved. This liquid was then analyzed by ICP-MS, with set blanks and standards. All samples were coupled with three commercially available multi-element standards: a Spex CertiPrep calibration standard (Claritas), and two CPI check standards (CPI-1 and CPI-2). Every element analyzed included calibration standards, check standards and blanks to ensure quality data collection and return of values within detection limits of 1ppb for water samples and 1ppm for shell samples. A regression line was fitted to this array of calibration points and the equation of this line was used to quantify unknown sample concentrations. Deviation of standards from the regression line was used to estimate analytical accuracy and analyses of reagent blanks were used to estimate lower limits of detection.

Water grab samples were collected throughout the hydrograph during large scale changes in discharge, once in the spring at Prentiss Gage and Cartoogechaye Creek and again in the fall at all three gaging stations and analyzed for anions and cations at the NBMG lab. These samples were filtered through 15 ml syringes with 0.45 µm Wattman filters and stored in 50 ml polypropylene vials. Both vials and syringes were cleaned with trace metal grade nitric acid in the lab prior to sampling and nitrile gloves were used to handle all equipment as well as during sampling and filtering to avoid contamination. Cation sampling vials were fixed with 2-3 drops of nitric acid in the lab, to resist against metal partitioning after sample collection. Samples were collected for both dissolved (filtered to 0.45 µm) and total (unfiltered) trace metals, with the dissolved samples being filtered in the field directly after collection. Automated Isco samplers, manufactured by Teledyne Isco, were installed at all sampling sites by the second storm event and water grab samples were collected from 500 ml polypropylene Isco bottles on the day following the storm event (Storm #2 – November 30, 2010 samples were collected from the Isco sample bottles on December 01, 2010). Water samples were filtered and acidified during the first sampling event, whereas the fall sampling event included acidified filtered and unfiltered samples in order to provide dissolved, suspended and total concentration comparisons.

Large-scale changes in discharge relating to rain events were targeted in water grab sampling with samples collected during the rise and fall of the hydrograph in order to develop an understanding of how these concentrations are changing with flow. During porewater sampling ambient baseflow conditions were targeted due to sampling methods requiring low stage conditions for collection of porewaters. Equipment blanks were analyzed at the beginning of every porewater sampling session in the lab to ensure no contamination of the sampling equipment had occurred. During the blanking process, deionized water was collected through syringes carried in the field along with sample syringes and ran through the same spectrometry procedures as the daily samples. In all cases the equipment blanks came back below detection showing no contamination existing from the sampling equipment.

Field sampling syringes were prepared for field sampling by cleaning and rinsing with deioned water and storing in sealed containers carried into the field which held samples until analysis could be completed. Sample replications were carried out at two separate sites to determine variability between samples; these samples were collected randomly three times from the same area normally sampled to produce a triplicate comparison sample and then in a transect spanning the width of the Little Tennessee River.

Hydrographs for all three sites were maintained during data collection and used for data interpretation including how changes in flow may relate to contaminant mobility and sources. The discharge summaries collected in real-time through USGS stream gages at all three study sites (nc.water.usgs.gov/) relate directly to turbidity values collected by the water quality sondes and should help develop an understanding of sedimentation and erosion rates both during storm events and ambient conditions. Overall these data observations provide insight into the state of water quality in the elktoe habitat, sedimentation over the 2010 water year and any imposing threats from elevated trace metals in the basin.

RESULTS

Little Tennessee River at Needmore: USGS gaging station # 03503000

The Little Tennessee River at Needmore gaging station was established by USGS on October 1, 1898. Needmore is a long term data collection station with over 110 years of stage and discharge data on file. This gage was established to collect data below the Franklin Dam on Lake Emory. It was chosen as the downstream collection site during this investigation because of its location nearest the confluence of the Little Tennessee River and Fontana Lake (Figure 1). There is also a Sutron rain gage mounted to the gage house at this site, which was used in combination with TVA's Franklin rain gage to obtain precipitation data throughout this study (Figure 3).

Precipitation data were calibrated and maintained as part of the long-term continuous data record for this station. During the 2010 water year three events exceeded 5 cm of rain, with numerous smaller events in the 2.5 to 4 centimeter range (Figure 3). High discharge events up to 283 cubic meters per second (m^3/s) were recorded at the Needmore gaging station in early Feburary 2010 along with a peak just below 255 m^3/s in late January 2010 (Figure 4). A third large event of 227 m^3/s occurred in late November (Figure 4). A gradual decrease in average discharges was recorded at Needmore from January to September, with discharge decreasing to 7 m^3/s during September and October (Figure 4). Several peaks rising between 28 and 34 m^3/s were common with rain events throughout the year (Figure 4).

Temperature readings recorded at the Needmore gaging station show a trend of increasing values from January 2010 to August 2010 and decreasing from August 2010 to

January 2011. Temperatures exceeded 30° C during August and fell below 0° C in January and December (Figure 5).

Turbidity values at this gaging station ranged from 0-10 NTUs on average during the winter months and often fell below detection limits (Figure 6). Some of the larger storm events exhibited turbidity values over 200 NTU. More commonly events reached turbidity values at or above 100 NTUs (Figure 6).

Dissolved oxygen was recorded at the Needmore gaging station using a luminescent dissolved oxygen (LDO) sensor and recorded in miligrams per liter (mg/L). Missing data seen in mid-June and August depict two events of LDO sensor failure that was repaired through HACH manufacturer warranty on both occasions. Dissolved oxygen values at this site ranged from 7 to 14 mg/L, increasing in the colder months and decreasing in warmer months (Figure 7).

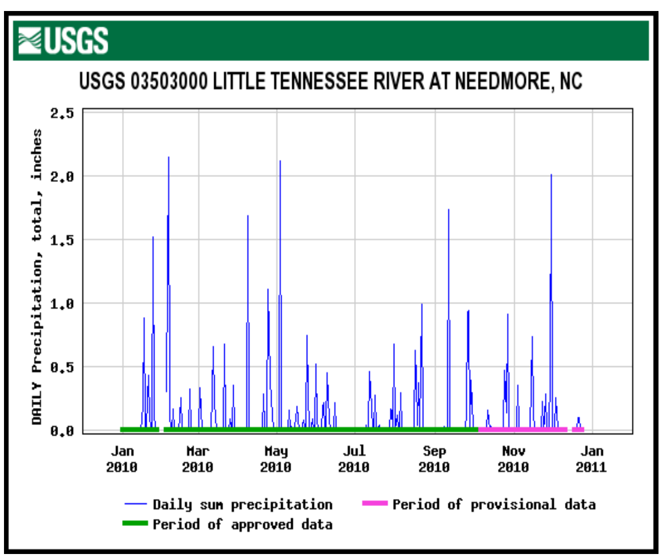

Figure 3. Precipitation at Needmore.

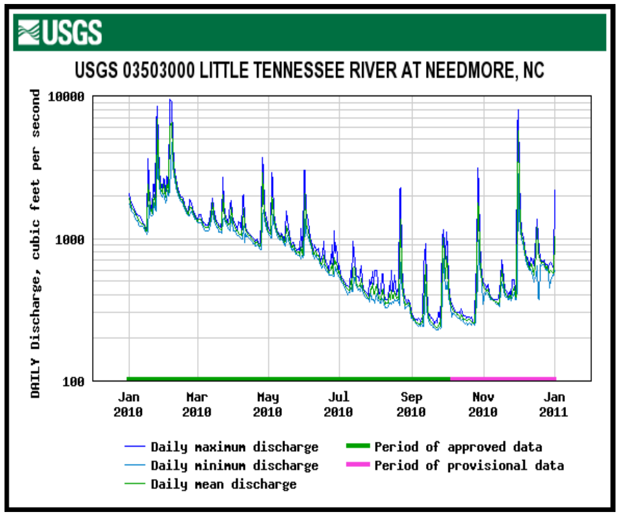

Figure 4. Discharge at Needmore.

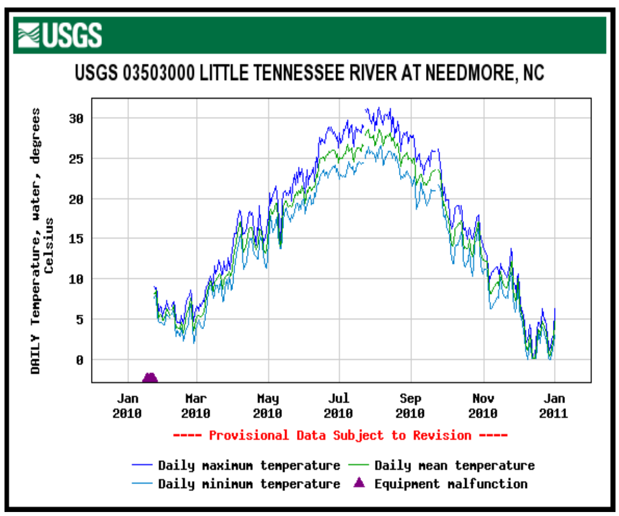

Figure 5. Temperature at Needmore.

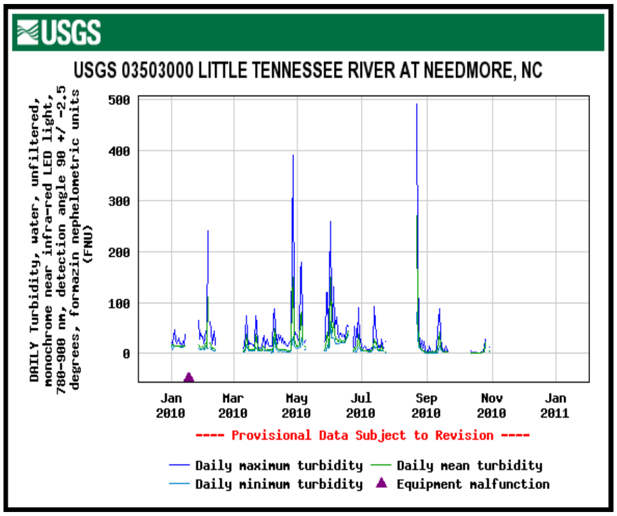

Figure 6. Turbidity at Needmore.

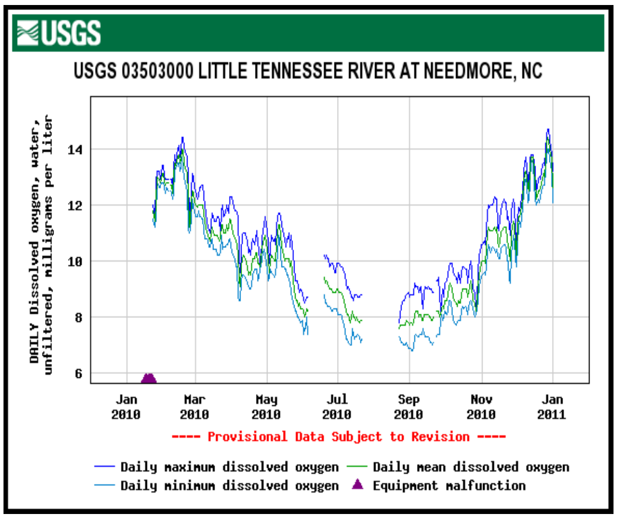

Figure 7. Dissolved oxygen at Needmore.

Little Tennessee River at Prentiss: USGS gaging station # 03500000

On October 1, 1898 the Prentiss gaging station began collecting discharge data. This site is maintained as a long term data collection station with over 110 years of stage and discharge data on file. Prentiss provides a representative example of the upstream conditions found on the Little Tennessee River due to its location upstream of the town of Franklin and the Lake Emory impoundment. Situated approximately 19 kilometers north of the Georgia state line, Prentiss is located above the confluence of Cartoogechaye Creek and the Little Tennessee River (Figure 2).

Discharge calculations were compiled by the staff at the USGS Water Science Field Office in Asheville, NC during this project and I assisted in data collection and compilation. Numerous high water events were recorded during the 2010 water year, including discharge levels just below 85 m^3/s in late January, early Feburary and early December (Figure 8).

Temperature data at the Prentiss gage ranged from a low of 1.5° C in January 2010 to a high of 27° C in August (Figure 9). Missing data in late May and June are due to sonde failure and replacement on two occasions where the water quality sondes were sent back to the manufacturer for repair. Data missing from late November to January are due to sonde failure and significant lag-time in obtaining a replacement probe at the end of 2010 (figures 9, 10 and 11). At the time of this publication, Coweeta Hydrologic Station is maintaining a sonde at this site and has collected data since January 2011. The station plans to continue collecting data through 2012 (Gragson 2008).

Turbidity data were collected at Prentiss using an automated, brushed self-cleaning infra-red turbidity probe on a HACH multi-sensor water quality sonde. Large spans of turbidity data were collected below-dectection limits as seen on Figure 10 in April, July-September and November-December. Turbidity grab samples collected at all three gaging sites and used for comparison to the water quality sondes during this project were used to determine that values below approximately 10 NTUs were beyond the detection limits of these probes.

Turbidity data were collected for two large events during this deployment, one in late January (01/27/2010 – 01/31/2010) and the other in late September (09/28/2010 – 10/02/2010); turbidity values reached 600 NTUs (Figure 10). Several smaller storms produced turbidity in excesses of 200 NTUs. Overall this upstream reach exhibited low-turbidity values (0-20 NTUs), except during high water events.

Dissolved oxygen was collected at the Prentiss gage using an LDO sensor which collected oxygen data in milligrams per liter (mg/L). Average values of LDO at this site were 10 mg/L, while values over 14 mg/L were reached in the colder months (Figure 11). Values below 4 mg/L were seen during warmer periods of early September and late October. Unfortunately, some of the warmer periods during June and July were missed due to probe failure, but consistent data through May and August show dissolved oxygen averaging 8 mg/L throughout these periods (Figure 11).

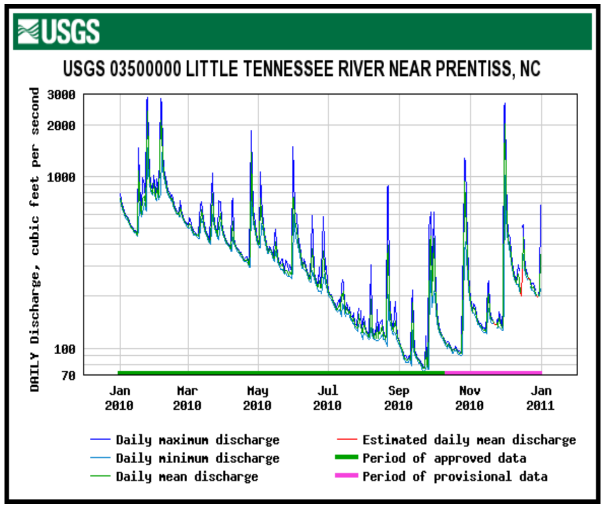

Figure 8. Discharge at Prentiss.

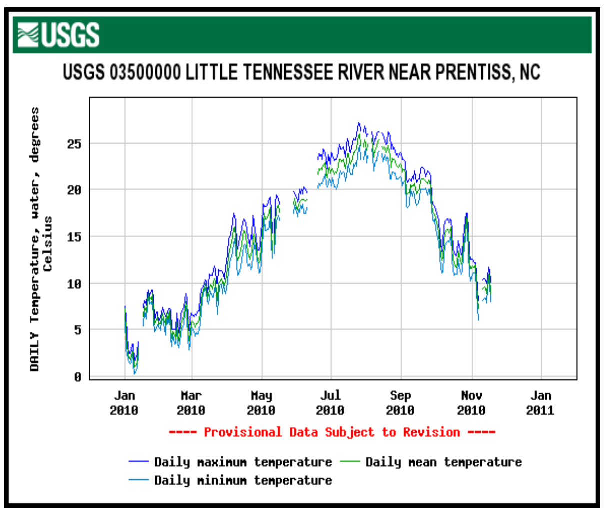

Figure 9. Temperature at Prentiss.

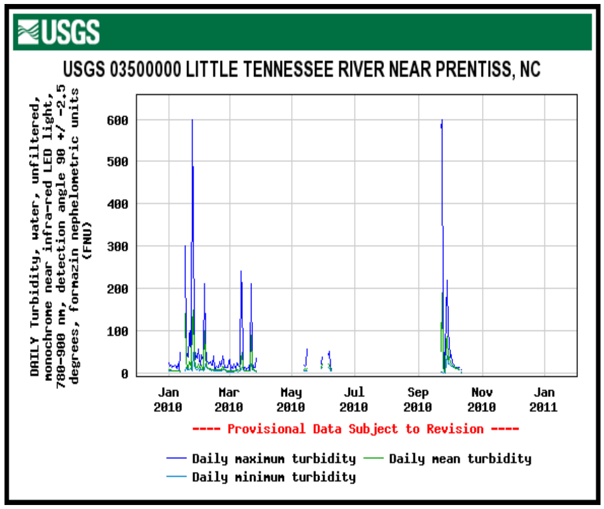

Figure 10. Turbidity at Prentiss.

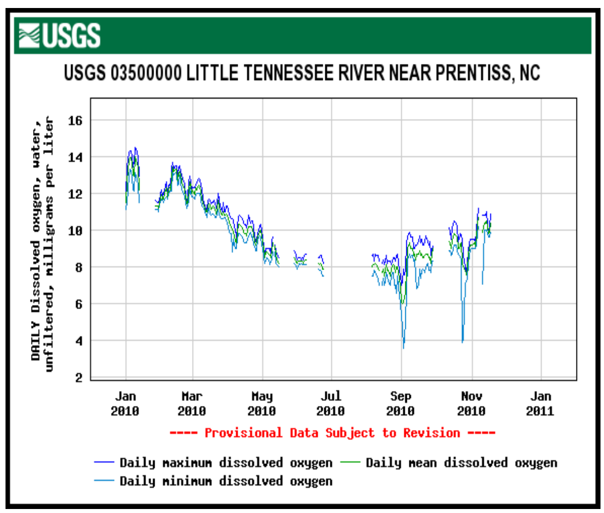

Figure 11. Dissolved oxygen at Prentiss.

<u>Cartoogechaye Creek at Franklin, NC: USGS gaging station # 03500240</u>

Cartoogechaye Creek is a tributary to the Upper Little Tennessee River located between the Prentiss and Needmore gaging stations (Figure 2). This gage has been a part of the stream gaging roster at USGS since June 1, 1949. The same sampling protocols were carried out at this site during the project in order to attain water quality data from the perspective of a tributary to the Upper Little Tennessee River.

Discharge levels during the 2010 water year at the Cartoogechaye Creek gaging station recorded discharge readings reaching 34 m^3/s in late January and early Feburary and 28 m^3/s during the high-water event of early December. A second set of water grab samples were collected using an automated Isco sampler installed at the Cartoogechaye Creek gaging station by the Coweeta Hydrologic Station during this earlier period. Discharges decreased to 0.85 m^3/s in the warmer summer months and numerous rises in discharge were recorded during rain events (Figure 12).

Temperature readings recorded at the Cartoogechaye Creek gaging station show values in excess of 25° C during warmer summer months and values below 5° C in Feburary. Temperatures down to 0° C were reached in early December (Figure 13).

Turbidity values at this tributary gaging station were often below detection limits. Numerous turbidity grab samples, collected and verified using field probes by the Coweeta Hydrologic Station staff, exhibited values below 10 NTUs (and often below detection). However, during some of the larger storm events turbidity values reached 100 NTUs. For example, back to back events in early October produced turbidity values around 250 NTUs (Figure 14).

Dissolved oxygen was recorded at the Cartoogechaye Creek gaging station using an LDO sensor and recorded in mg/L. Average dissolved oxygen values at this site were 11 mg/L, with values reaching 14 mg/L in the colder month of December and dropping below 4 mg/L in late June-early July (Figure 15).

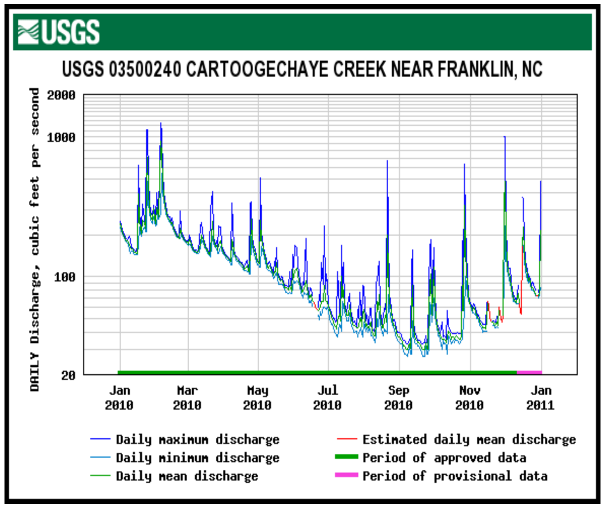

Figure 12. Discharge at Cartoogechaye.

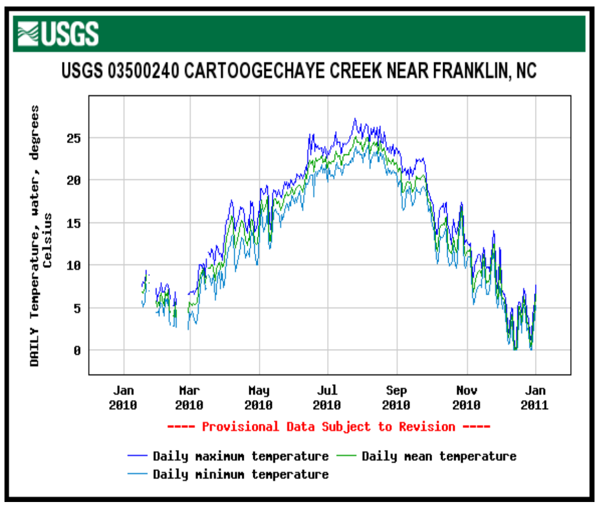

Figure 13. Temperature at Cartoogechaye.

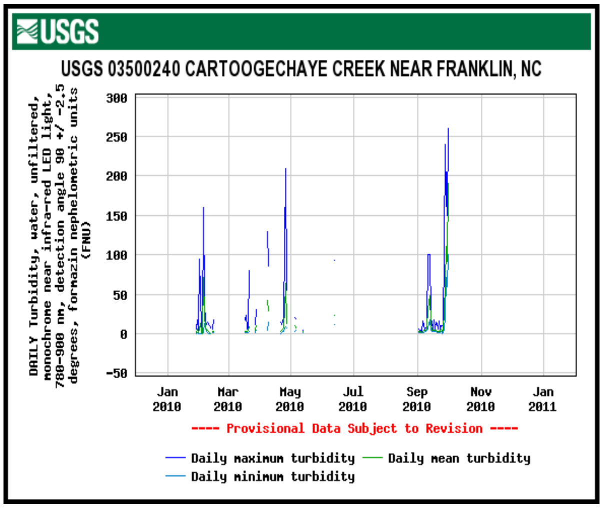

Figure 14. Turbidity at Cartoogechaye.

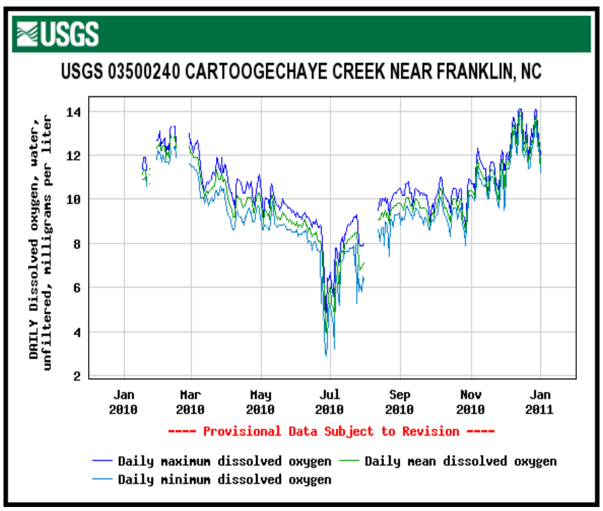

Figure 15. Dissolved oxygen at Cartoogechaye.

Shell Chemistry

Elktoe mussel shells were collected during this project from the Upper Little Tennessee and the Tuckasegee Rivers by survey crews assisting the NC Wildlife Commission on routine annual surveys (Table 2). Table 2 provides the approximate ages of the mussel shells as determined from observations of the annual growth rings.

Table 2. Age of analyzed elktoe mussel shells from the Little Tennessee and Tuckasegee Rivers.

Tuckasegee River	Shell Age	Little Tennessee River	Shell Age
03.17.2010.01	9	03.17.2010.15	9
03.17.2010.02	7	03.17.2010.16	9
03.17.2010.03	8	03.17.2010.17	6
03.17.2010.04	6	03.17.2010.18	8
03.17.2010.05	6	03.17.2010.19	7
03.17.2010.06	8	03.17.2010.20	6
03.17.2010.07	7	03.17.2010.21	8
03.17.2010.08	7	03.17.2010.22	5
03.17.2010.09	7	03.17.2010.23	6
03.17.2010.10	7	03.17.2010.24	7
03.17.2010.11	5	03.17.2010.25	7
03.17.2010.12	8	03.17.2010.26	6
03.17.2010.13	7	–	–
03.17.2010.14	6	–	–

For the mussel shells analyzed, age to concentration graphs were compiled for both the Little Tennessee and Tuckasegee rivers to (1) determine the total accumulation of trace metals over time, and (2) provide a general comparison between the Tuckasegee River elktoe mussel populations which currently appear to be thriving with the Little Tennessee populations which are in decline. Figures 19 through 24 show copper, lead, and zinc concentrations for all shells observed from both rivers. Chromium and nickel concentrations were also determined for these shell samples due to their elevated concentrations in river water samples; however, the measured concentrations were below detection limits of 1 ppm in all samples.

Mussels observed from the Little Tennessee River ranged in age from approximately 5 to 9 years old with an average age of 7. In the Tuckasgee River the mussels ranged in age from approximately 5 to 9 years old with an average age of 7.1. Therefore, the age ranges of the two rivers were highly comparable; however, no major differences in metals concentrations from 5 to 9 years of age were apparent. The average ages of mussel shells analyzed during this project show that these mussels were living in the rivers between 5 and 9 years ago and represent concentration values accumulating from approximately 2001-2005, giving an observation of mussel shells which would have been present in the basin during recently observed declines. Trace metal concentrations analyzed in the mussel shells are greater than values determined for overlying waters and less than values determined for sediments in the basin. The values are also higher than concentrations seen through porewater analysis. These observations suggest that the mussels are accumulating the trace metal concentrations through time from water column contamination experienced during storm events.

A median test (Siegel and Castellan 1988) was used to test whether copper, lead and zinc concentrations in shells in the Tuckasegee River differed from that in shells in the Little Tennessee River. This nonparametric test was used because neither set of data conformed to assumptions of normality and because the two populations differed considerably in the shape of their respective frequency distributions. Median test results for copper were P=0.036, suggesting that copper levels were significantly higher in shells from the Tuckasegee (Figure 16). Elktoe mussel populations from these stocks appear to be thriving and expanded according to survey results from the past several years carried out by the NC Fish and Wildlife Commission (Fraley 2010). Copper levels accumulated in the mussel shells over the past 6-9 years range from 7-38 ppm in the Little Tennessee River and 15-42 ppm in the Tuckasegee River (Figures 19 and 20).

Lead median test results also suggested that levels were significantly higher in the Tuckasegee River, $P<0.001$ (Figure 17). While the zinc median test resulted in $P=0.680$ demonstrating little evidence of a difference in zinc levels (Figure 18). Lead levels accumulated in the mussel shells over the past 6-9 years range from 2-3 ppm in the Little Tennessee River and 2-81 ppm in the Tuckasegee River (Figures 21 and 22). Again concentrations are higher in shells from the Tuckasegee River than from the Little Tennessee River.

Zinc concentration values exhibit little difference between shells from the Little Tennessee River versus shells from the Tuckasegee River, with the exception of shell 03.17.2010.03. This particular shell has an overall concentration of 48 ppm, a level much higher than any other sample collected. Several samples exhibit zinc concentrations in the 6-10 ppm range; 10 ppm is the next highest concentration below the 48 ppm value (Figures 23 and 24). Chromium and nickel concentrations were below detection limits in mussel shells from both the Upper Little Tennessee and Tuckasegee Rivers.

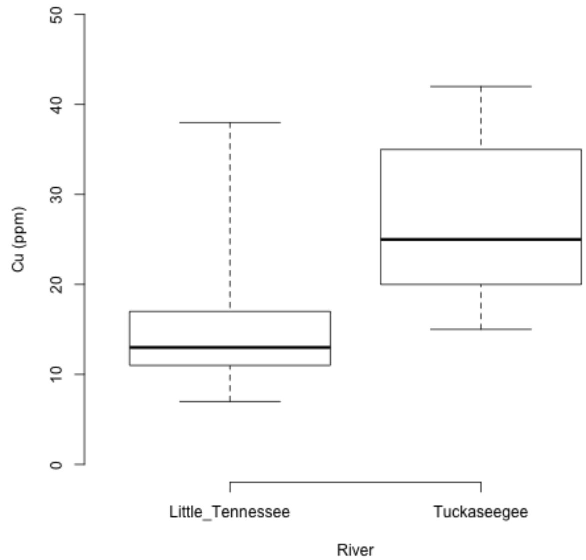

Figure 16. Box plot for copper concentrations in mussel shells.

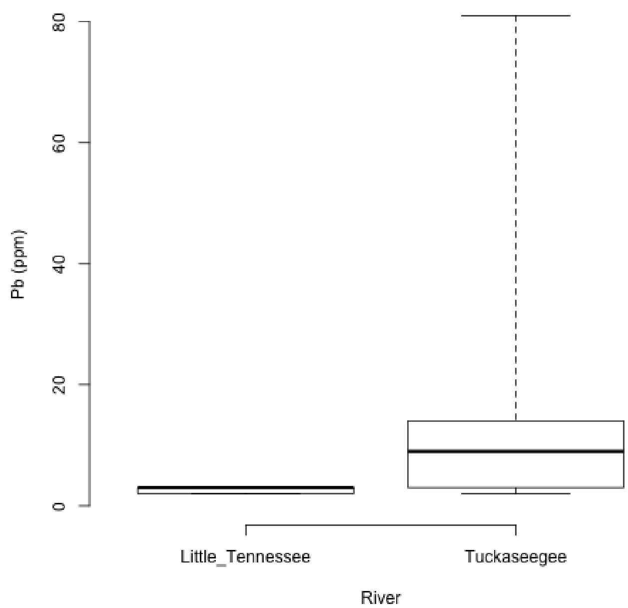

Figure 17. Box plot for lead concentrations in mussel shells.

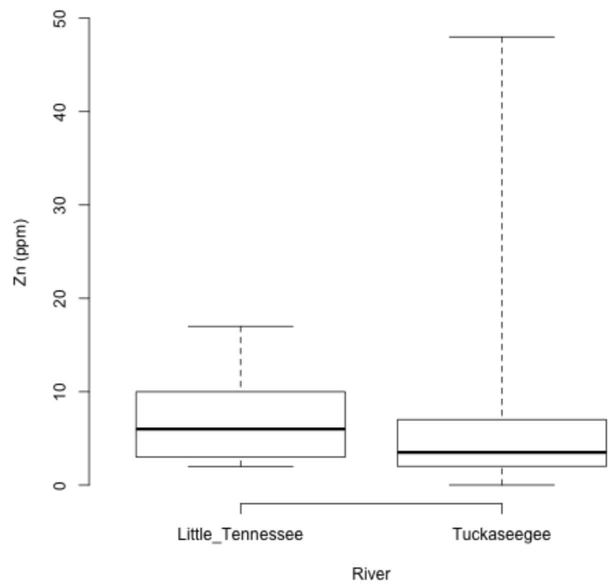

Figure 18. Box plot for zinc concentrations in mussel shells.

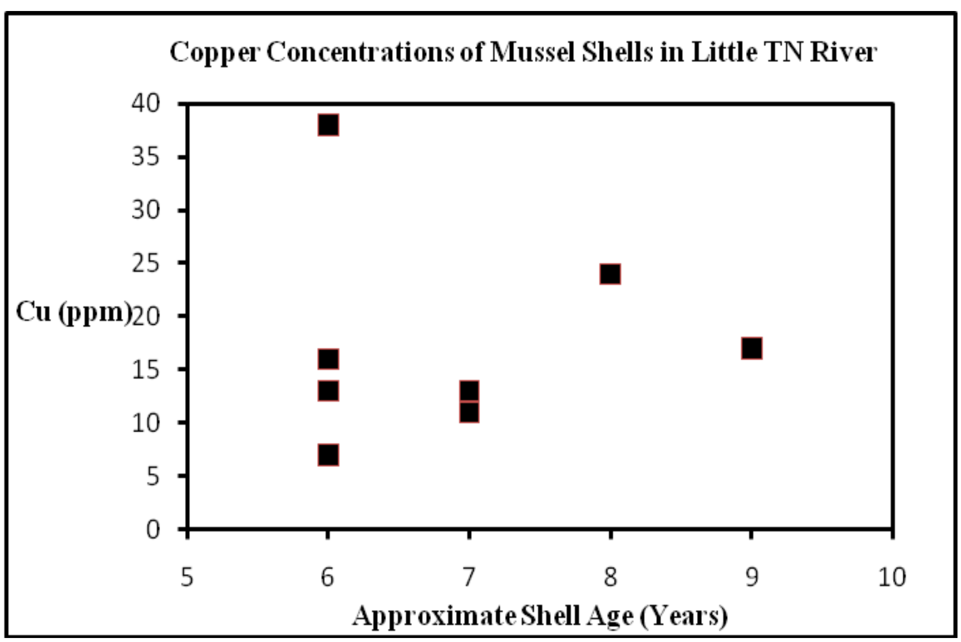

Figure 19. Copper in Little Tennessee River mussel shells.

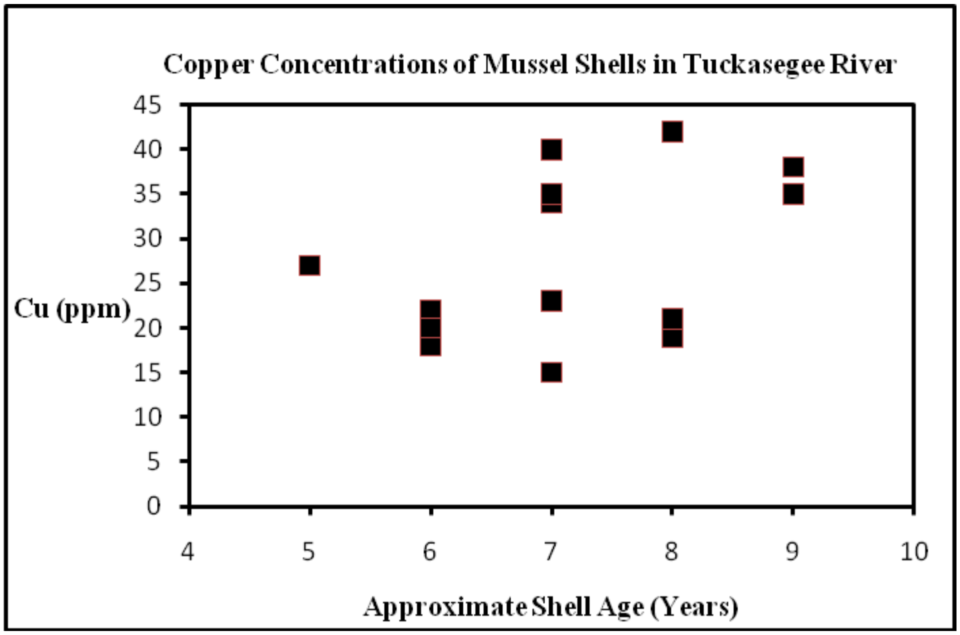

Figure 20. Copper in Tuckasegee River mussel shells.

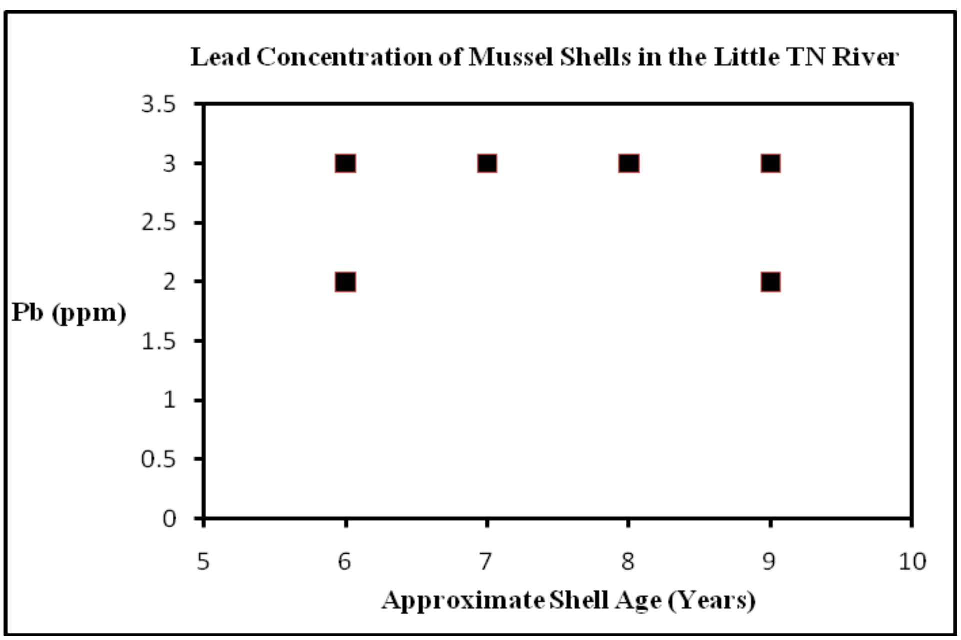

Figure 21. Lead in Little Tennessee River mussel shells.

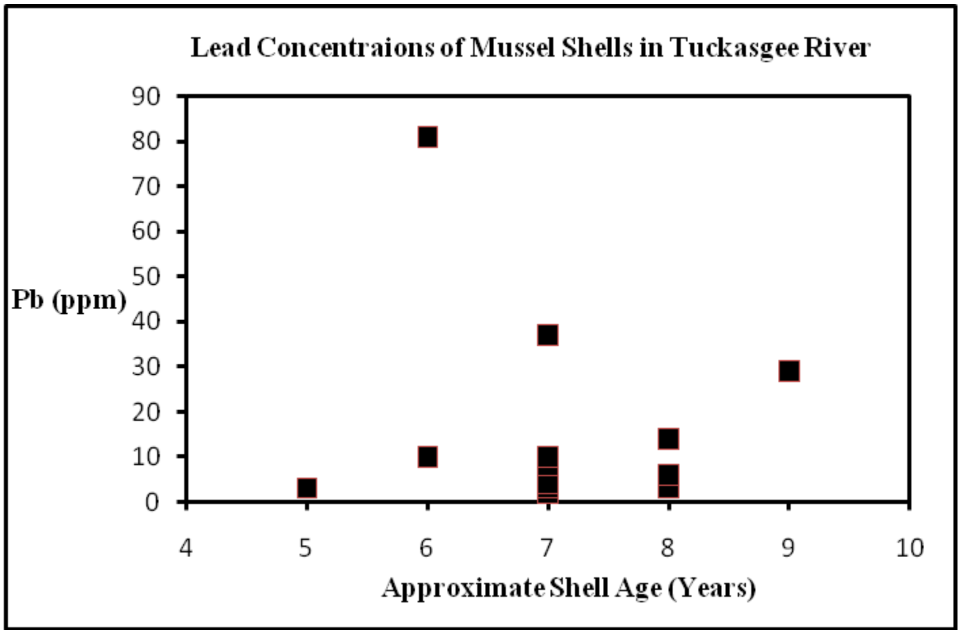

Figure 22. Lead in Tuckasegee River mussel shells.

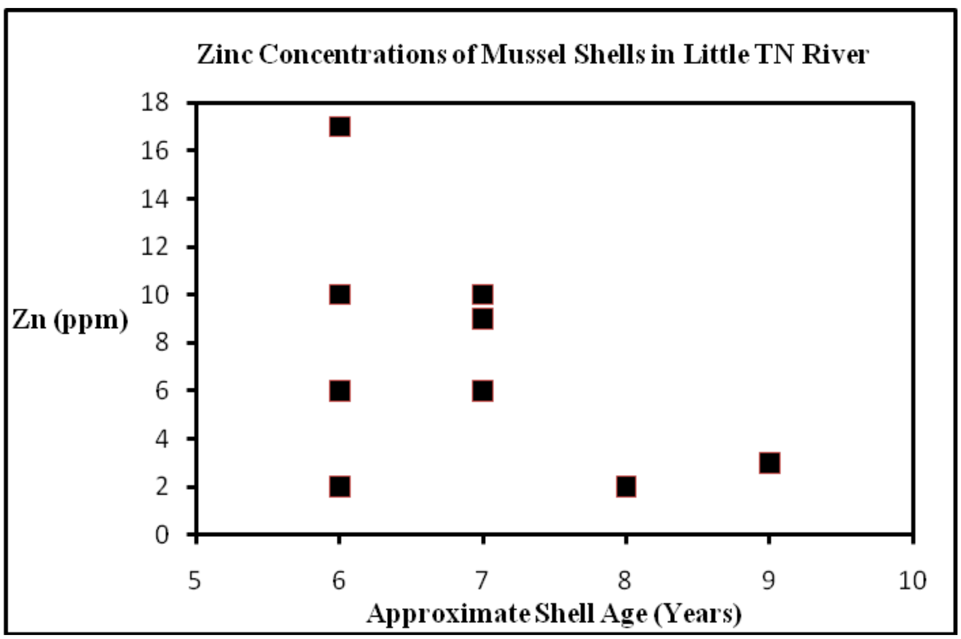

Figure 23. Zinc in Little Tennessee River mussel shells.

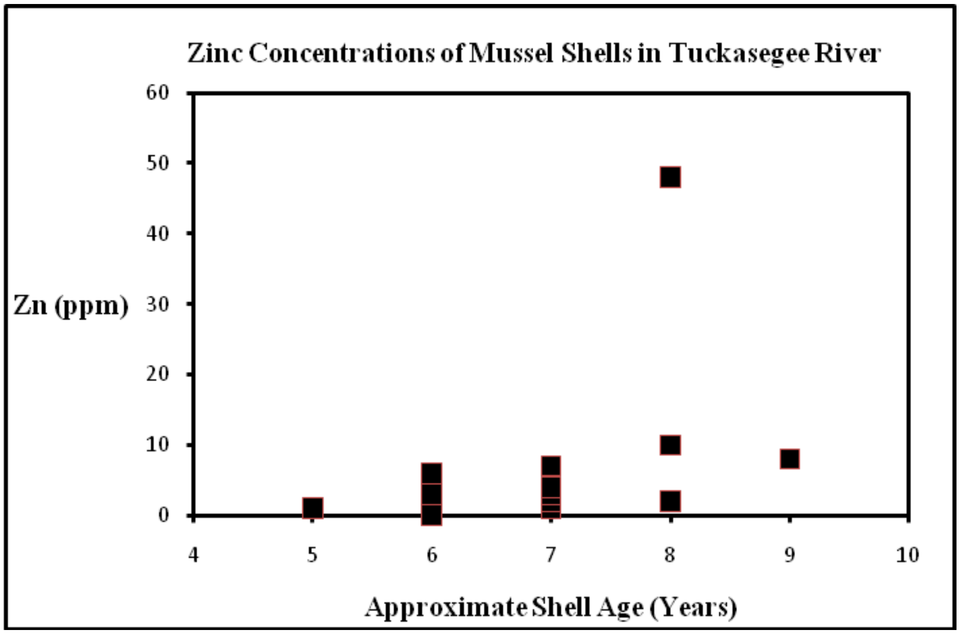

Figure 24. Zinc in Tuckasegee River mussel shells.

Water Trace Metal Chemistry

ICP-MS analysis was carried out on water grab samples uniformly collected during two separate storm events to examine trace metal concentration changes as a function of discharge. The following results show concentrations measured at the three sites relative to the threshold of possible threat to aquatic life.

Storm #1: (5/31 - 6/1/2010): Hydrology

Storm #1 was a spring storm event resulting from 2 cm of rainfall over a 24 hour period. The annual recurrence interval for precipitation in this region is 7.26 cm over a 24 hour period with a 90% confidence interval (nws.noaa.gov). Therefore, a rain event over three magnitudes larger than this event can be expected to occur annually with a 90% confidence interval according to historical conditions. This storm produced a peak discharge of 4 m^3/s at Cartoogechaye Creek and is well within the historical annual mean discharge values for the site (Figure 26). The two-year recurrence interval at Cartoogechaye Creek is 53.3 m^3/s (Table 3), making Storm #1 a small event for Cartoogechaye Creek.

Peak discharge at Prentiss was 40.5 m^3/s, which is well above the historical anuual mean (Figure 28) and on the lower end of historical annual peak flows on record (Figure 27). The two-year recurrence interval for storms at the Prentiss gage is 91.4 m^3/s (Table 3), making Storm #1 an annual to multi-annual event. Discharge levels at Prentiss rose significantly higher than Cartoogechaye due to the southern location of the storm event. The discharge peak at Prentiss lasted over 4 hours with discharge increasing by 26 m^3/s. Base flow conditions at Prentiss, noted two weeks prior during a dry period, were 10.2 m^3/s. The discharge peak at Cartoogechaye lasted 3.5 hours and the discharge only increased 0.85 m^3/s higher than base flow conditions.

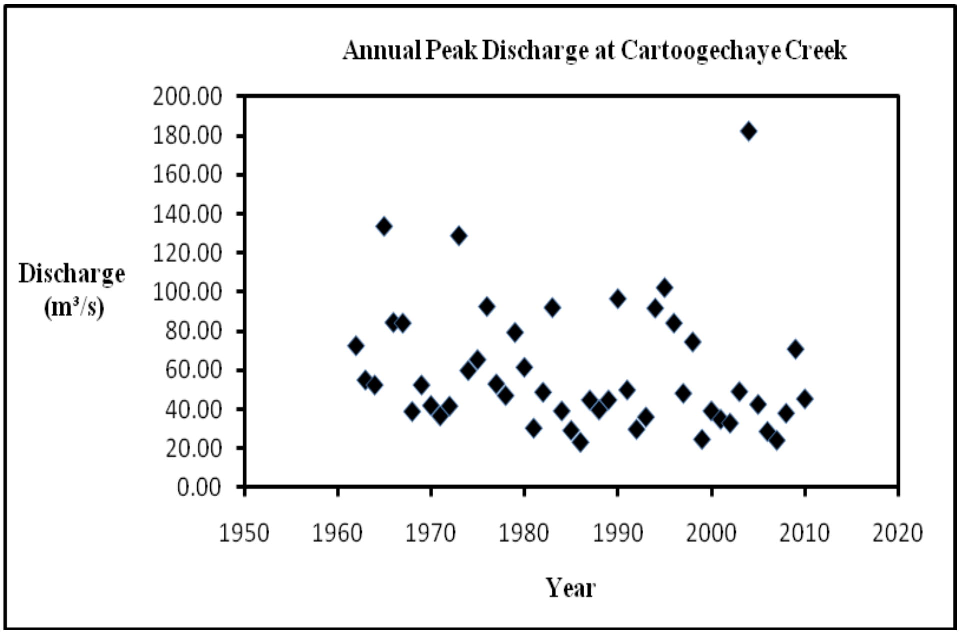

Figure 25. Annual peak discharge at Cartoogechaye Creek.

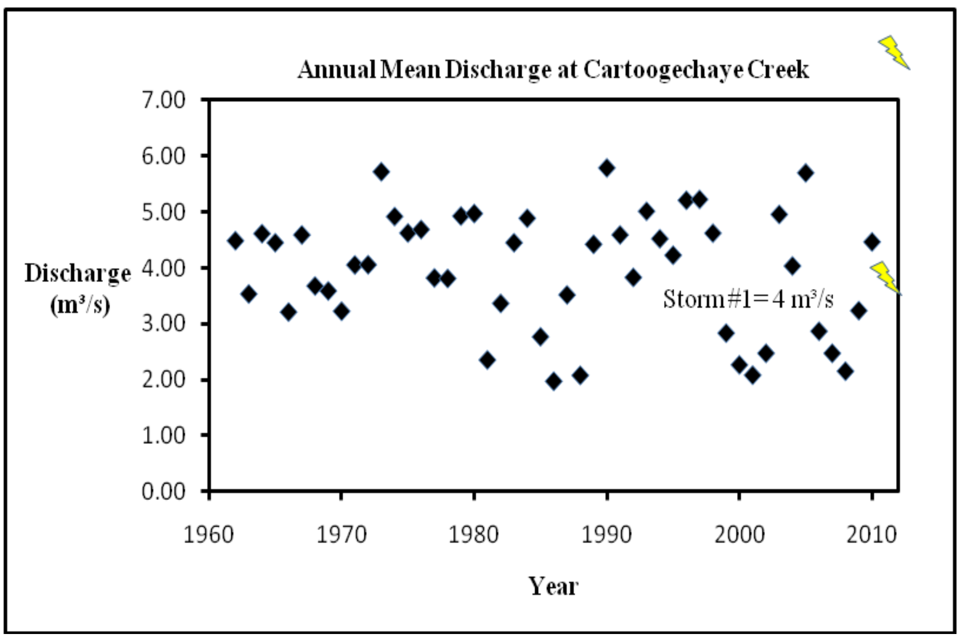

Figure 26. Annual mean discharge at Cartoogechaye Creek

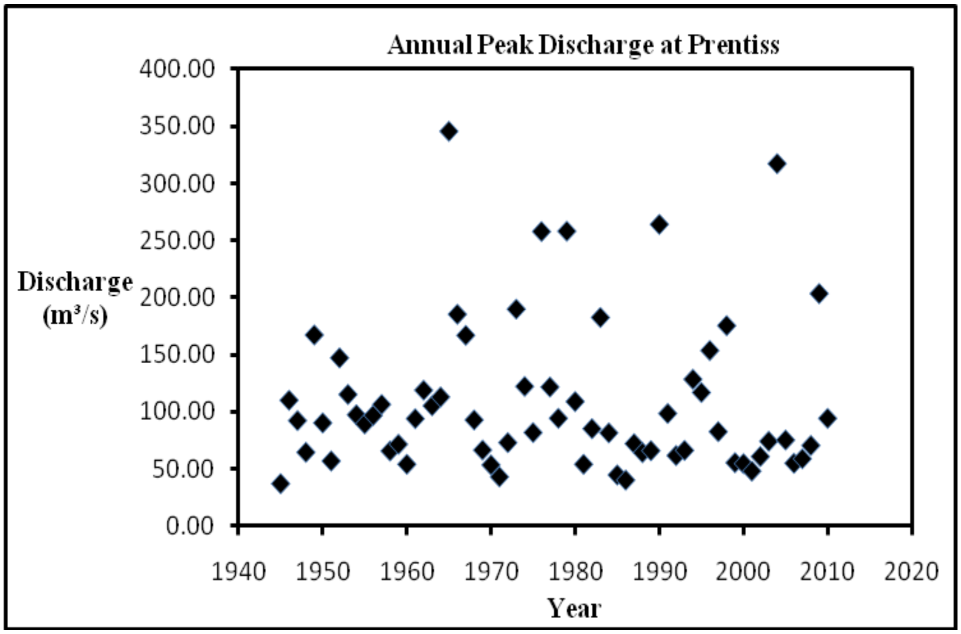

Figure 27. Annual peak discharge at Prentiss gage.

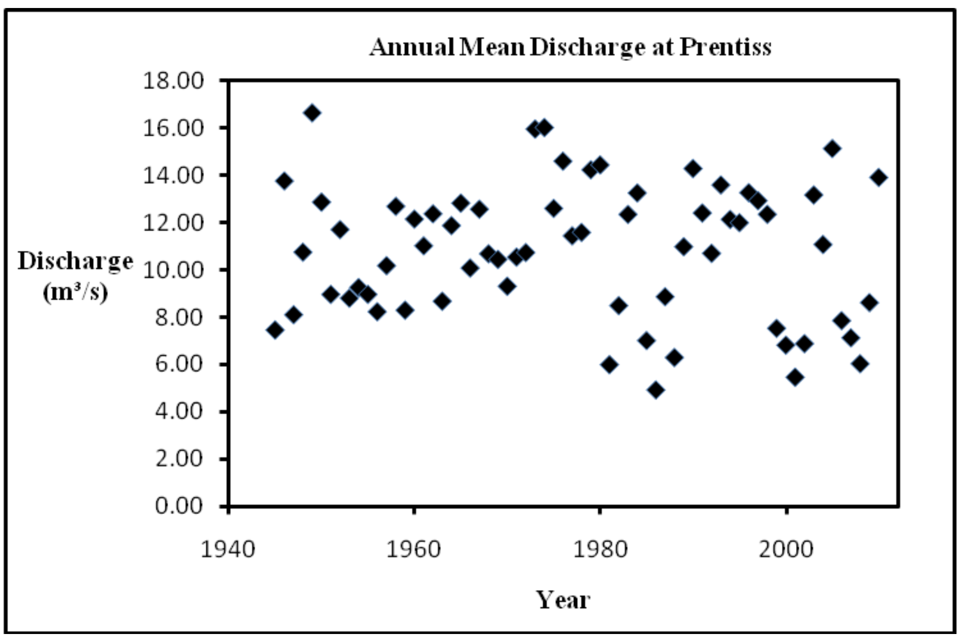

Figure 28. Annual mean discharge at Prentiss gage.

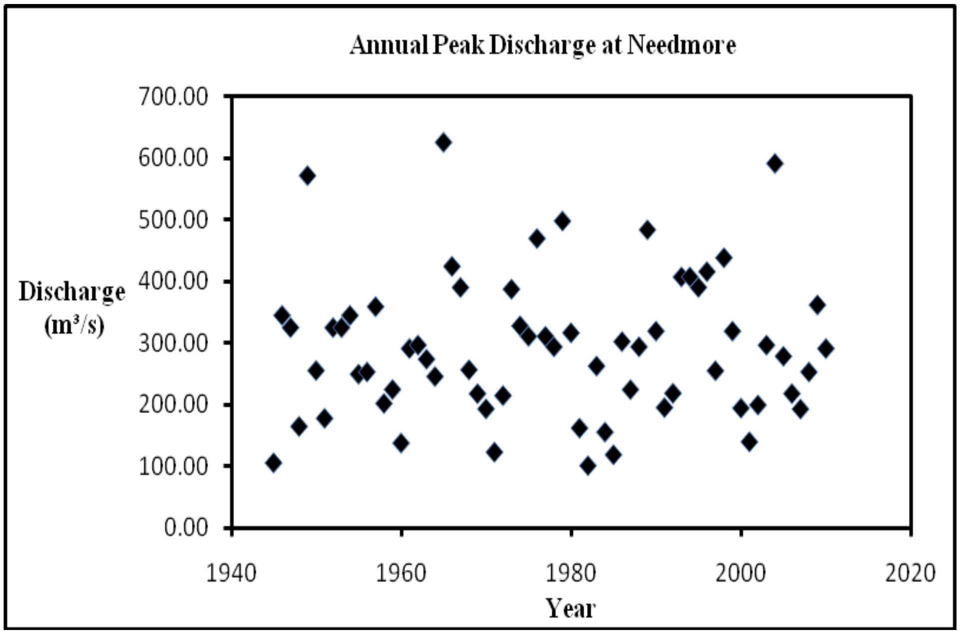

Figure 29. Annual peak discharge at Needmore gage.

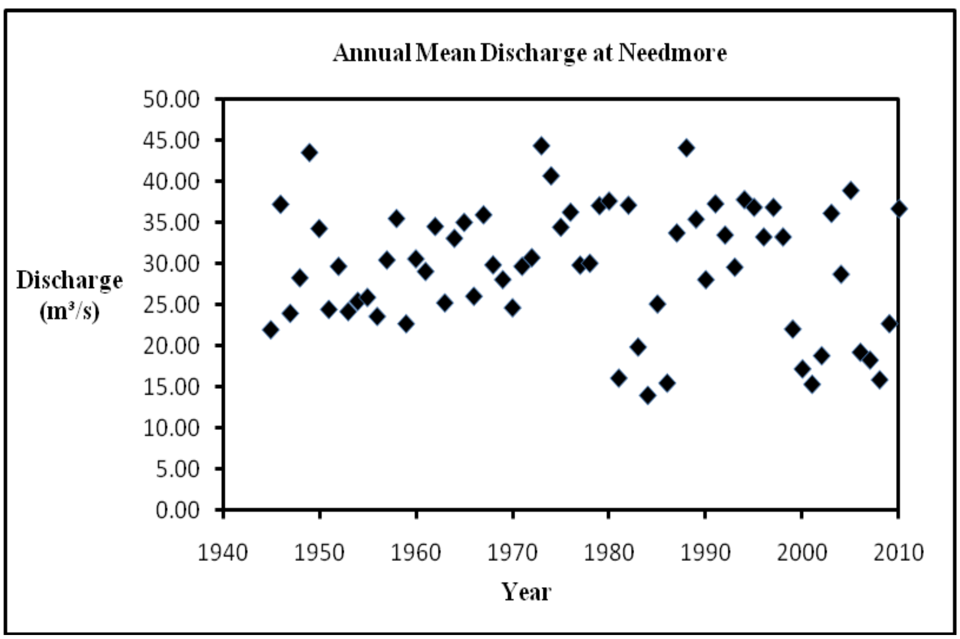

Figure 30. Annual mean discharge at Needmore gage.

Table 3. Flood frequency intervals at gaging stations. Compiled using Log Pearson III Estimates (Weaver 2009).

Station	2-Year Event (m^3/s)	5-Year Event (m^3/s)	10-Year Event (m^3/s)	25-Year Event (m^3/s)	50-Year Event (m^3/s)	100-Year Event (m^3/s)
Cartoogechaye Creek	53.5	82.9	105.8	138.4	165.8	195.8
Little TN River at Prentiss	91.4	143.8	185.4	245.6	297.2	353.8
Little TN River at Needmore	273.4	384.9	455.6	245.6	605.6	667.9

Water Chemistry: Cartoogechaye Creek

Dissolved copper concentrations were mostly below detection limits during Storm #1 at Cartoogechaye Creek (Figure 31). Chromium, lead and zinc also were below detection limits throughout the flood at both the Cartoogechaye Creek and Little Tennessee River at Prentiss gages. Dissolved nickel concentrations at Cartoogechaye Creek were all below the 1 µg/L detection limit.

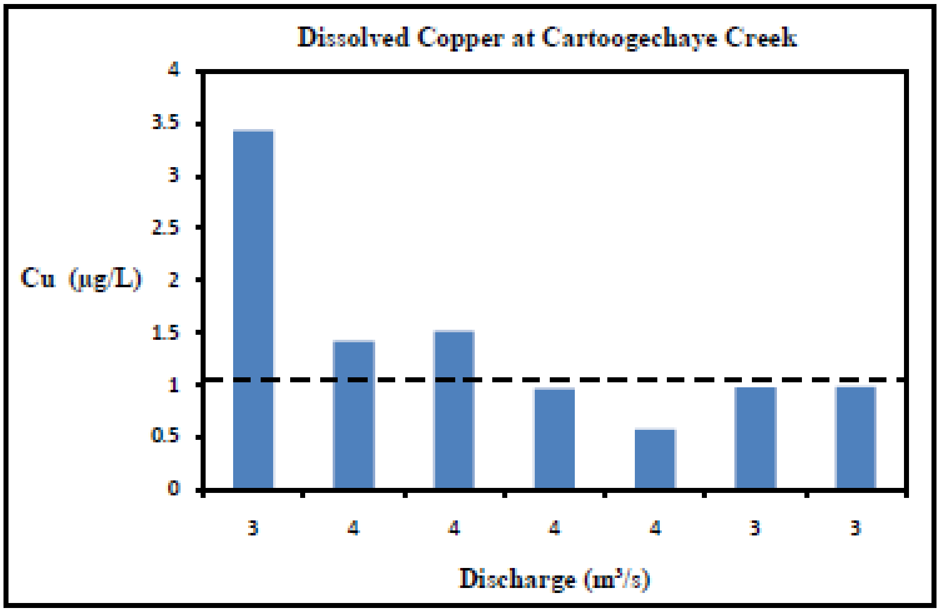

Figure 31. Storm #1 dissolved copper concentrations for Cartoogechaye Creek; with calibration detection limit denoted by dashed line.

Water Chemistry: Prentiss

Dissolved copper concentrations at Prentiss ranged from 0.60 to 11 µg/L (Figure 32). The 11 µg/L sample was an upper end outlier, with concentration levels over two orders of magnitude higher than the other samples. This sample was collected at the end of the falling limb of the hydrograph, and was observed to be 11 µg/L at a discharge of 18 m^3/s. This discharge represents less than half the peak flow and is nearing pre-storm event discharge levels recorded at 14.7 m^3/s. Dissolved nickel concentrations at Prentiss remained below the 1 µg/L detection limits of the ICP-MS for most samples; all sample concentrations were lower than the NC water standard limits of 88 µg/L for unfiltered samples during storm #1.

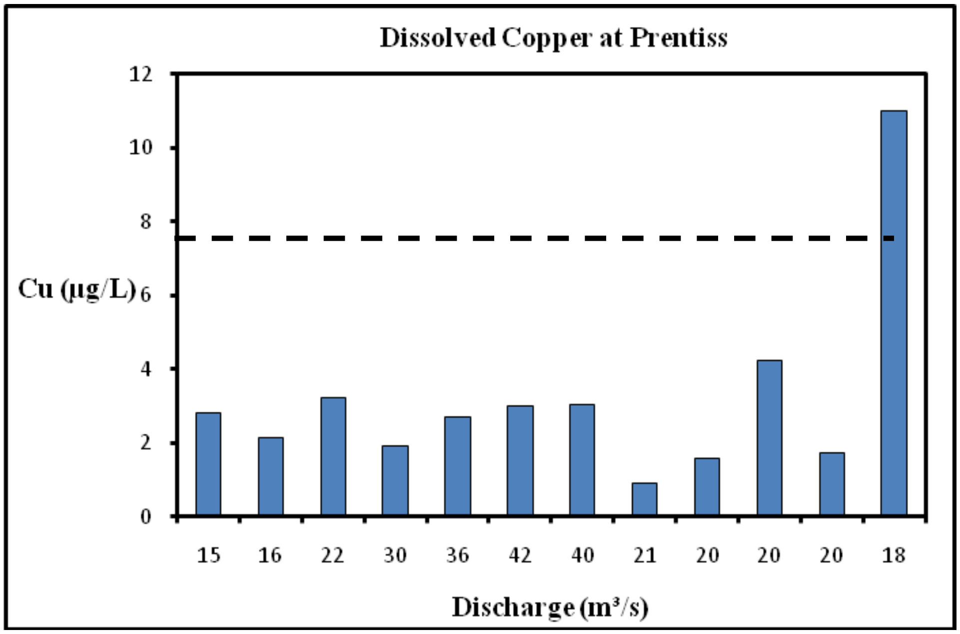

Figure 32. Storm #1 dissolved copper concentrations for Little Tennessee River at Prentiss; 7 µg/L water quality standard for unfiltered samples denoted by dashed line.

Storm #2 (11/30 – 12/01/2010): Hydrology

Storm #2 consisted of a 5 cm rainfall event over a 48 hour period, a value that was equalled or exceeded only three times in the 2010 water year (Figure 3). The annual recurrence interval for precipitation in this region is 7.26 cm over a 48-hour period with a 90% confidence interval (nws.noaa.gov). In other words, in a typcial year it can be expected to rain 7.26 cm at least once over a 48-hour period based on historical precipitation trends.

This storm produced a peak discharge of 28.3 m^3/s at Cartoogechaye, 74.8 m^3/s at Prentiss and 226.5 m^3/s at Needmore. The 2-year recurrence intervals for these sites are 53.5 m^3/s at Cartoogecahye, 91.4 m^3/s at Prentiss and 273.4 m^3/s at Needmore (Table 3).

At Cartoogechaye, discharge remained above 17 m^3/s for 9 hours. Prentiss sustained discharges above 56.6 m^3/s for 9 hours and Needmore remained above 170 m^3/s for over 12 hours. This was one of the three largest storm events during the 2010 water year, all of which were produced from 5 - 5.6 cm of rain and resulted in discharges from 226.5 m^3/s to 283.2 m^3/s (Figure 4).

<u>Water Chemistry: Cartoogechaye Creek</u>

The action level of total recoverable (unfiltered) copper for freshwater aquatic life in NC is 7 µg/L (NCDENR 1998). Two of the total recoverable copper samples collected at Cartoogechaye exceeded this guideline (Figure 33). One being on the rising limb of the hydrograph and the second being the last sample observed on the falling stage of the hydrograph. An additional three were close (5.72, 5.92 and 6.53 µg/L) to exceeding this threshold during Storm #2.

Total nickel concentrations were below detection limits across the hydrograph at Cartoogechaye and Prentiss, except for the low total recoverable values indicated in figure 34, which are well below the water supply standard in NC of 25 µg/L (NCDENR 1998). Chromium and lead concentrations were below detection limits at Cartoogechaye and Prentiss during Storm #2. Zinc concentrations analyzed at Cartoogechaye were well under the 50 µg/L water supply standard with only one 42.79 µg/L sample getting close to the standard at Cartoogechaye (Figure 35).

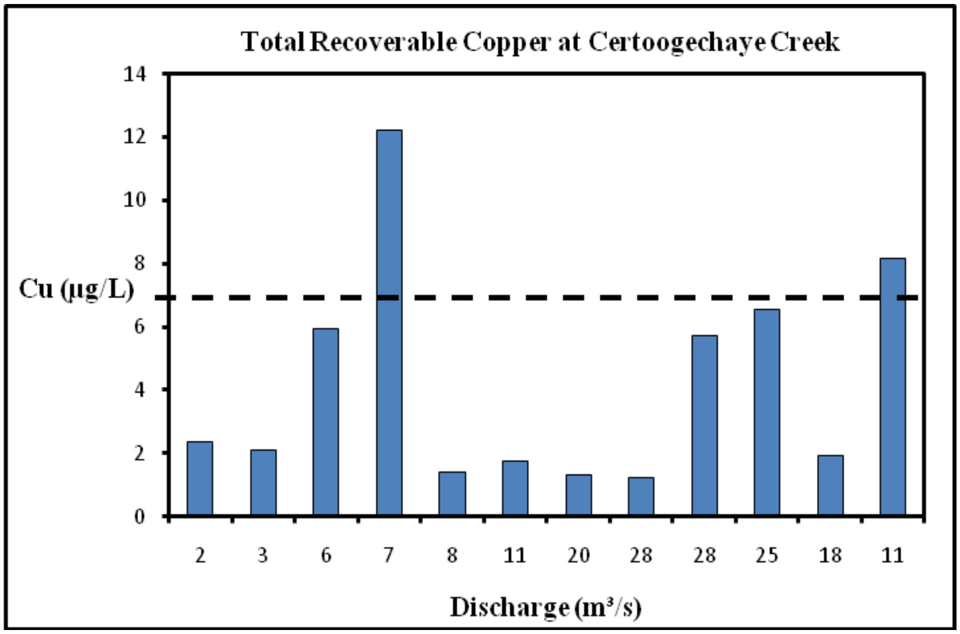

Figure 33. Storm #2 total recoverable copper concentrations for Cartoogechaye Creek; 7 µg/L water quality standard denoted by dashed line.

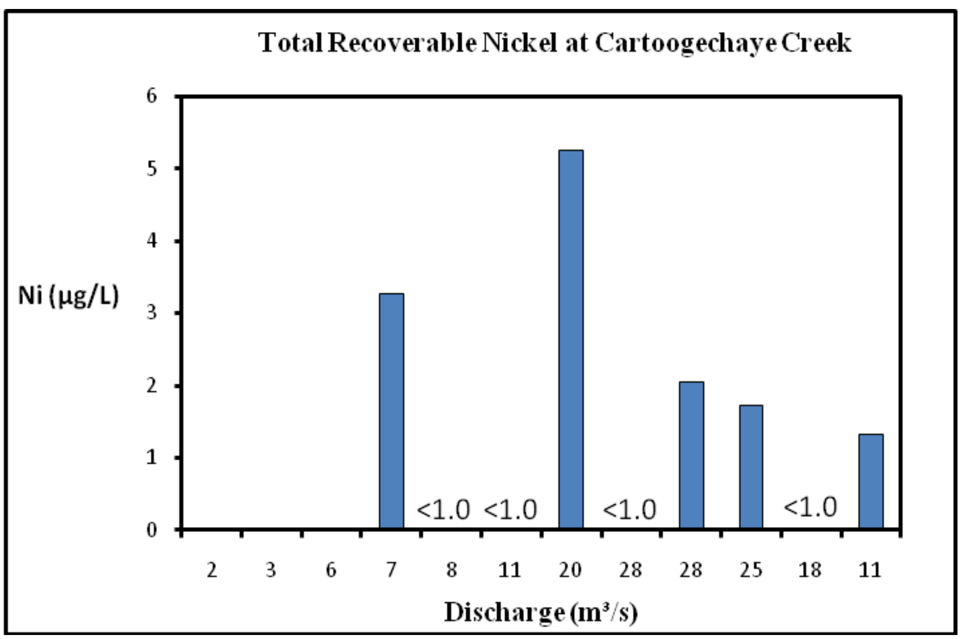

Figure 34. Storm #2 total recoverable nickel concentrations for Cartoogechaye Creek.

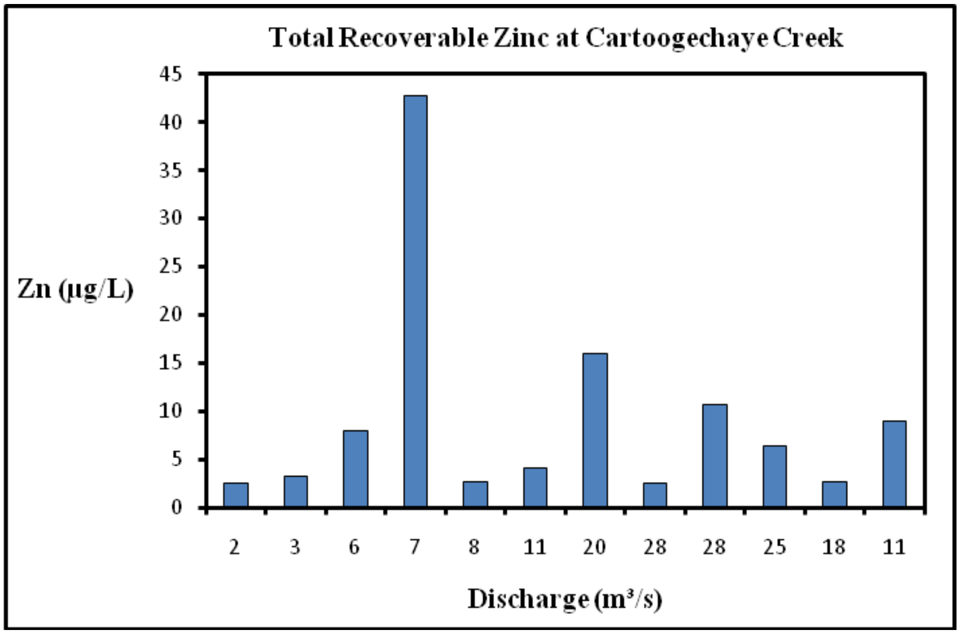

Figure 35. Storm #2 total recoverable zinc concentrations for Cartoogechaye Creek.

Water Chemistry: Prentiss

Two total recoverable copper samples exceeded the freshwater aquatic life guideline at Prentiss during storm #2, one being at the very beginning of the storm and the other on the peak (Figure 36). Total recoverable Zinc concentrations remained below freshwater aquatic guidelines for Storm #2 at Prentiss (Figure 37).

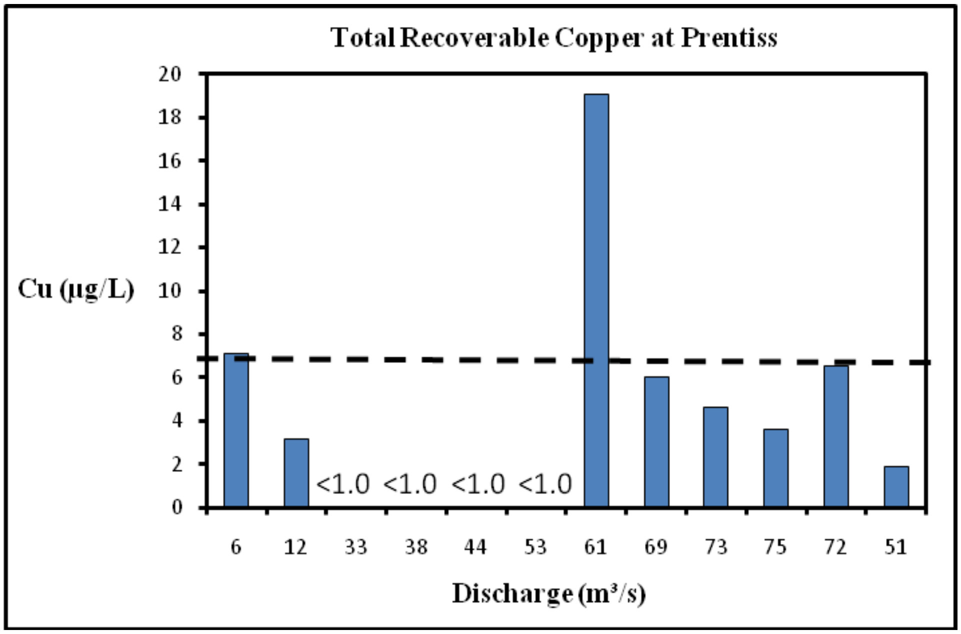

Figure 36. Storm #2 total recoverable copper concentrations for Little Tennessee River at Prentiss; 7 µg/L water quality standard denoted by dashed line.

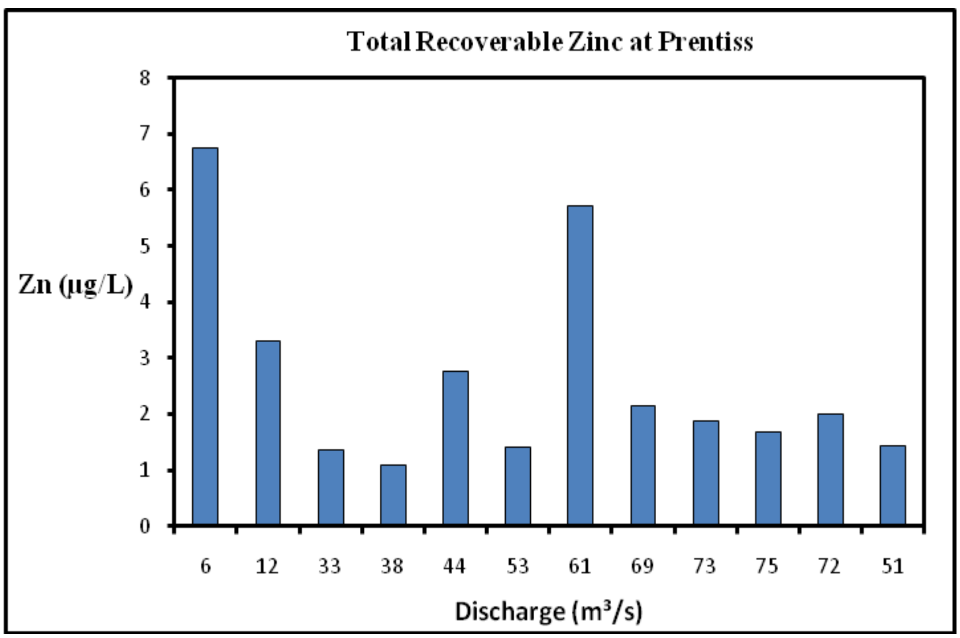

Figure 37. Storm #2 total recoverable zinc concentrations for the Little Tennessee River at Prentiss.

Water Chemistry: Needmore

Fifty percent of the samples at the Needmore gage exhibited total recoverable copper concentrations above the 7 µg/L threshold (Figure 38). Total dissolved copper at Needmore exceeded the action level of copper for freshwater aquatic life at 75% of sites, while two of the three samples that did not exceed the 7 µg/L standard were observed at 6.96 and 6.64 µg/L (Figure 39). The remaining sample that did not exceed the guideline was the baseline sample collected at the beginning of the flood. Storm #2 sampled at Needmore provided a dramatic view of the increase in copper concentrations related to the rise in discharge at this site (Table 4).

None of the zinc samples analyzed for Storm #2 at Needmore, gage exceeded the freshwater aquatic life threshold for zinc of NC at 50 µg/L (NCDENR 1998) in the dissolved or total recoverable phase (Figures 40 and 41).

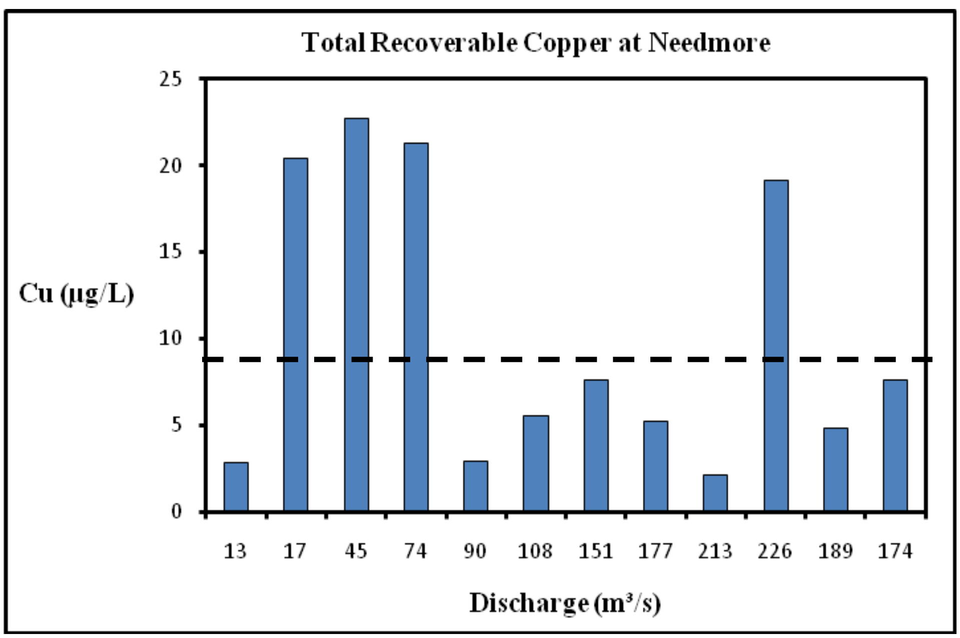

Figure 38. Storm #2 total recoverable copper concentrations for Little Tennessee River at Needmore; 7 µg/L water quality standard denoted by dashed line.

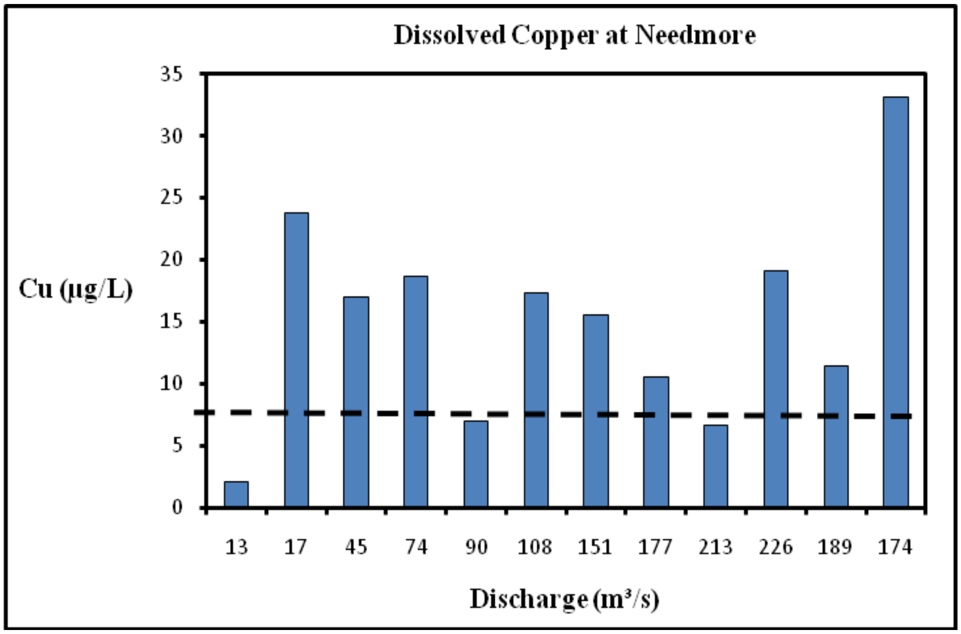

Figure 39. Storm #2 dissolved copper concentrations for Little Tennessee River at Needmore; 7 µg/L water quality standard denoted by dashed line.

Table 4. Copper concentrations in µg/L for Storm #2 at Needmore.

Sample #	Total Recoverable Copper	Dissolved Copper
1	2.84	2.07
2	20.38	23.75
3	22.70	16.98
4	21.25	18.67
5	2.92	6.96
6	5.54	17.37
7	7.65	15.61
8	5.25	10.50
9	2.15	6.64
10	19.12	19.10
11	4.87	11.39
12	7.65	33.18

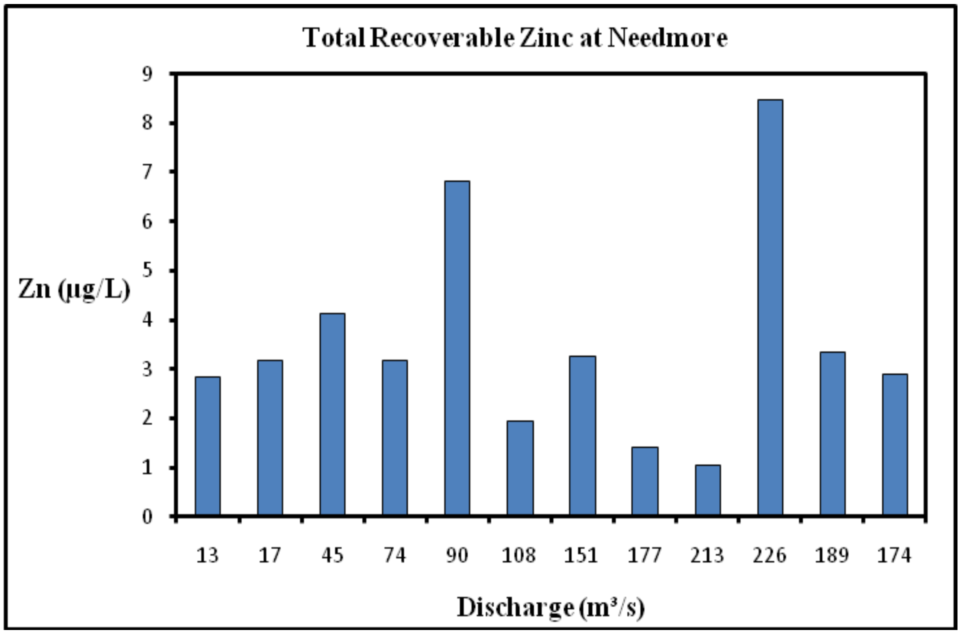

Figure 40. Storm #2 total recoverable zinc concentrations for Little Tennessee River at Needmore.

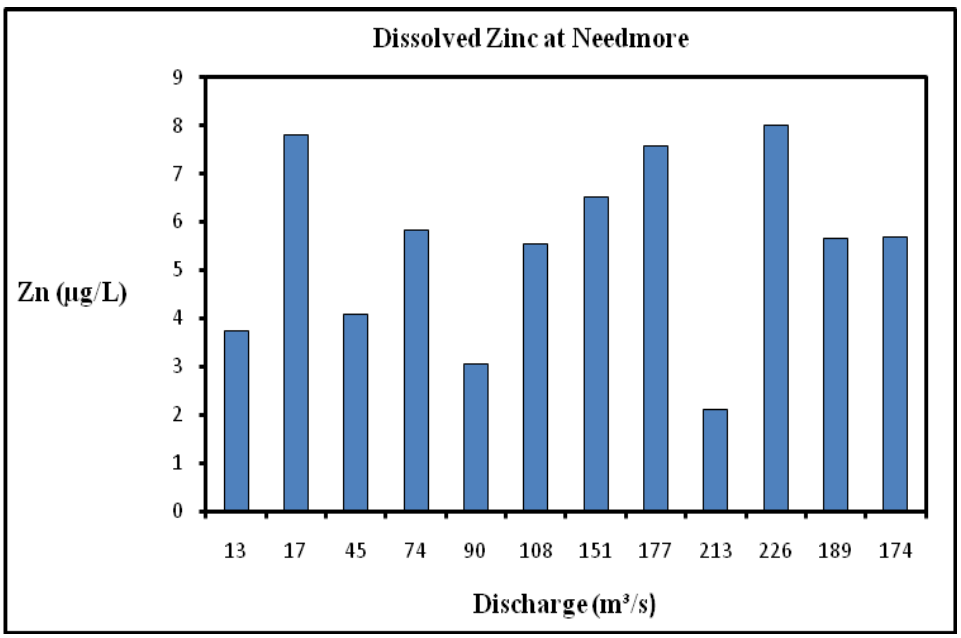

Figure 41. Storm #2 dissolved zinc concentrations for the Little Tennessee River at Needmore.

Water Chemistry Additional Elements

Many elements measured during water analysis on the ICP-MS during this project were below detection limits and proved to currently be at safe levels in the sampled conditions. These elements included: barium, boron, cobalt, chromium, lithium, molybdenum, lead, titanium, tin and antimony.

Porewater Sampling

Porewater samples collected in 0-3 cm, 7-10 cm and overlying waters all show copper levels well below the 23 µg/L EC 50 limit for glochida (Wang 2007). Only one sample analyzed exceeded the 7 µg/L NC aquatic life standard (Figure 42). The majority of these samples were observed below 1 µg/L (Tables 5 and 6).

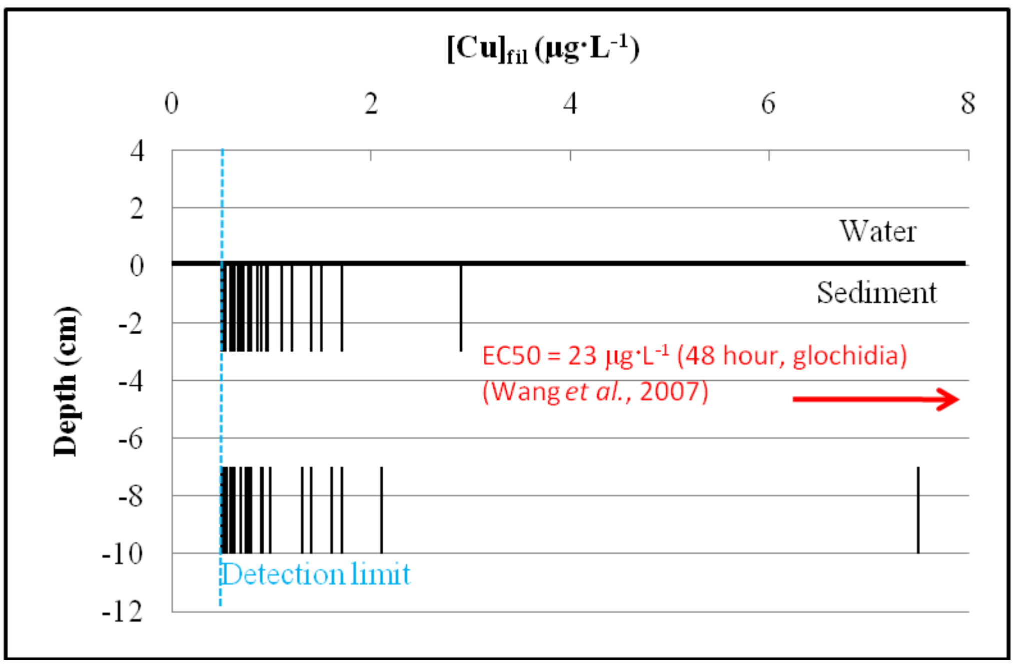

Figure 42. Filterable copper concentrations (in micrograms per liter) in overlying water and porewater (from Little Tennessee River Mussel Project Update Report by Sharon Fitzgerald- January 2011).

Table 5. Filterable copper concentrations ($\mu g \cdot L^{-1}$) in samples of overlying water and porewater from eight sites between Lake Emory and Lake Fontana (Fitzgerald 2011).

	Filterable copper ($\mu g \cdot L^{-1}$)				
	5-Aug-10	**15-Sep-10**	**17-Sep-10**	**28-Oct-10**	**8-Dec-10**
Little Tennessee River at Watauga Creek near Franklin, NC					
Overlying water	0.57	0.77	–	1.2	0.51
0-3 cm	<1.0	0.76	–	<.50	0.63
7-10 cm	<1.0	<1.0	–	7.5	<.50
Little Tennessee River below HWY 28 near Franklin, NC					
Overlying water	1.1	0.87	–	1.3	<.50
0-3 cm	0.66	<1.0	–	0.94	1.2
7-10 cm	<1.0	<1.0	–	0.98	0.89
Little Tennessee River above Cowee Creek near Franklin, NC					
Overlying water	0.88	0.77	–	1.2	<.50
0-3 cm	<1.0	0.5	–	0.89	1.2
7-10 cm	<1.0	<1.0	–	0.79	1.3
Little Tennessee River at Lucky Creek near Franklin, NC					
Overlying water	0.63	0.72	–	1.3	0.63
0-3 cm	0.54	0.61	–	1.5	0.71
7-10 cm	0.69	0.58	–	1.4	0.63
Little Tennessee River at Tellico Creek near Almond, NC					
Overlying water	0.77	–	0.71	1.1	<.50
0-3 cm	<1.0	–	0.59	2.9	0.71
7-10 cm	<1.0	–	<1.0	<.50	1.4
Little Tennessee River at Lost Cove near Almond, NC					
Overlying water	0.88	–	0.76	1.3	0.61
0-3 cm	0.69	–	<1.0	0.78	0.96
7-10 cm	<1.0	–	0.77	0.74	<.50

	Filterable copper ($\mu g \cdot L^{-1}$)

	5-Aug-10	15-Sep-10	17-Sep-10	28-Oct-10	8-Dec-10
Little Tennessee River at Needmore, NC					
Overlying water	0.65	–	0.93	1.3	<.50
0-3 cm	<1.0	–	<1.0	0.52	1.4
7-10 cm	0.89	–	0.5	<.50	0.76
Little Tennessee River at Burningtown Creek near Almond, NC					
Overlying water	–	–	0.7	1.3	<.50
0-3 cm	–	–	0.71	1.7	0.63
7-10 cm	_	_	<1.0	1.6	2.1

Table 6. Filterable copper concentrations ($\mu g \cdot L^{-1}$) from Little Tennessee River Mussel Project Update Report (Fitzgerald 2011). Equipment blank measured <0.5 $\mu g \cdot L^{-1}$ Cu.

Filterable Copper ($\mu g \cdot L^{-1}$)			
Little Tennessee River below HWY 28 near Franklin, NC (small radius samples)			
Sample	Overlying Water	0 – 3 cm	7 – 10 cm
1	<0.50	1.2	0.89
2	<0.50	0.96	–
3	<0.50	1.1	0.91
Little Tennessee River at Lost Cove near Almond, NC (small radius samples)			
Sample	Overlying Water	0 – 3 cm	7 – 10 cm
1	0.61	0.96	<0.50
2	<0.50	0.79	1.7
3	<0.50	0.86	1.4
*Little Tennessee River at Needmore, NC			
Sample	Overlying Water	0 – 3 cm	7 – 10 cm
A	<0.50	0.69	0.63
B	<0.50	0.59	0.91
C	<0.50	<0.50	<0.50
D	<0.50	<0.50	<0.50
E	<0.50	<0.50	<0.50

* Transect of equidistant points from left bank (A) to right bank (E)

Sample replicates for site one showed no localized variability for overlying waters, 0.06 µg/L variability between 0-3 cm samples and 0.02 µg/L variability between 7-10 cm samples. Sample replicates ran for site two showed a 0.11 µg/L range between overlying water samples, a 0.17 µg/L range between 0-3 cm samples and a 1.3 µg/L range between 7-10 cm samples. The transect samples showed no difference between overlying water samples, 0.19 µg/L for 0-3 cm samples and 0.41 µg/L for 7-10 cm samples across the width of the river (Table 6). None of the samples analyzed fell into a range in which the level of this variability would place them outside of water quality guidelines. Overall, the blanks and replicate samples analyzed for QA/QC during this process show no contamination of samples analyzed and replication samples show little (1.2 µg/L maximum) variability between two sets of triplicate samples.

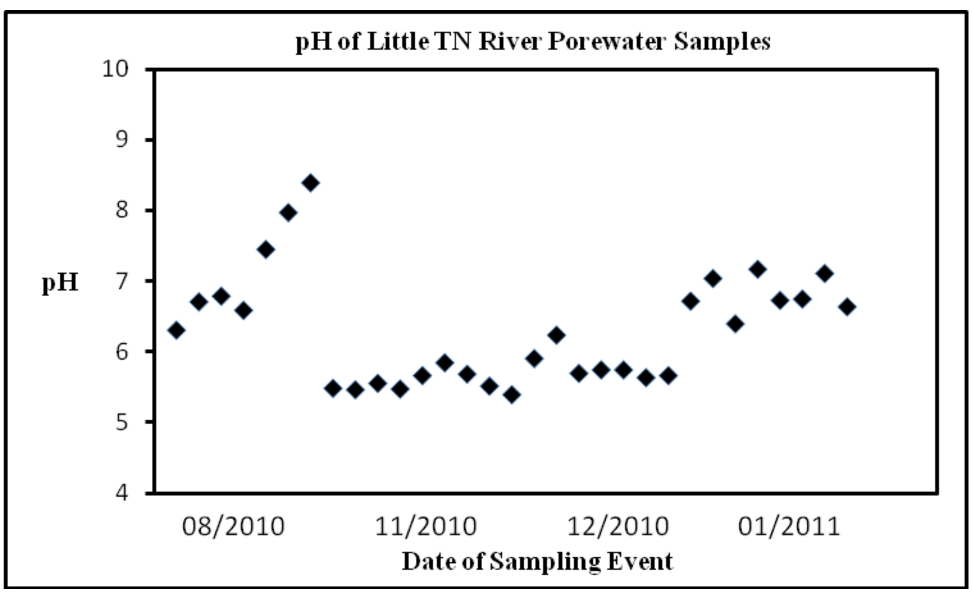

Figure 43. pH of Little Tennessee River porewater samples.

pH data collected during porewater sampling across the Little Tennessee River shows several sites approaching the 5.5 pH threshold level for sustaining aquatic life

(Borden and Behrooz 2008). Several (15/32) samples dropped below a pH of 6 and 20 % of the 32 samples collected were below a pH of 5.5. These samples were collected during base flow conditions and do not represent the occurrence many local streams have of pH dropping during increases in discharge (NCDENR 1997).

DISCUSSION

Elktoe mussel populations have rapidly declined since hurricanes Ivan and Francis in 2004. The large decline seen across the Upper Little Tennessee River basin has not been observed in the Tuckasgee River system where populations appear to be increasing. Annual mussel surveys and intensive surveying around the demolition of the Dillsboro Dam on the Tuckasegee River have produced higher than previously recorded population counts for elktoe mussels in the Tuckasegee River, while routine monitoring in the Upper Little Tennessee River since 2004 has shown continually decreasing elktoe mussel population counts (Fraley 2010).

Although no direct causal mechanism has been shown to explain the population declines in the Upper Little Tennessee River, a possible stressor is the remobilization of sediment-borne contaminants from either Lake Emory or other areas of the Little Tennessee River basin. The potential of trace metals to have negatively affected elktoe mussels is supported by recent studies showing concentrations of copper, zinc, nickel, chromium, and lead in the sediments of Lake Emory and the Upper Little Tennessee River exceeding probable effects thresholds cited by MacDonald (2000) (Miller 2010). Copper, in particular, is a potential stressor due to its known toxicity to mussels (Wang 2006, 2010; Strayer 2008; Luoma and Rainbow 2008).

<u>Water Quality Probe Data</u>

Water quality sondes collected data at all three sites during 2010, producing data on the aquatic habitat elktoe mussels are exposed to on an annual basis. Temperature data collected at both Prentiss and Cartoogechaye Creek exhibited values increasing to 26° C and decreasing below 0° C (Figures 9 and 13). Dissolved oxygen at Cartoogechaye decreased below the 5.0 mg/L threshold for freshwater aquatic life (NCDENR 1998) for a two week period in late June / early July 2010 (Figure 15). The Prentiss gage site also exhibited a decrease below the freshwater aquatic life standard in early September and late October (Figure 11). Turbidity ranges at Prentiss were often hard to quantify due to consistent probe failure issues, but data were consistent from January 2010 to April 2010 and exhibited values consistently below 50 NTUs during ambient conditions, but increasing to 600 NTUs during storm events. Multiple smaller events were also captured with turbidity observances of 200 NTU (Figure 10). Also at the Needmore gage turbidity often increased well above the 10 NTU NC water quality standard for trout waters and the 25-50 NTU standard for freshwater aquatic life (NCDENR 1998). Cartoogechaye Creek exhibited very low turbidity levels throughout the year, often producing values below detection limits; however, data were collected for three storm events which produced turbidity peaks exceeding 150, 200 and 250 NTUs respectively (Figure 14).

Dissolved oxygen at Needmore remained above the 5.0 mg/L aquatic life threshold (NCDENR 1998) as seen in Figure 7. Temperature ranges at the Needmore gage exhibited values reaching temperatures from a high of 31° C in August 2010 to below 0° C in December 2010 (Figure 5). Although mussels are known for being able to tolerate low temperature extremes, often going into torpor and slowing down or shutting off many of their costly biologic functions, temperatures over 30 degrees have been shown as lethal to several juvenile mussel species. Dimmock and Wright (1993) found a 96-hour LT50 value of 31.5 ºC for two freshwater mussel species sampled and further complications during anoxic conditions, with 7-10 day old juvenile mussels unable to survive 24-hours in anoxic conditions (Farris and Van Hassel 2007). Although standards for mussel species do not currently exist, bivalves have been shown to be highly sensitive to changes in their environment (Augspurger 2003). These data exhibit dissolved oxygen, temperature and turbidity limits which could be harmful to survivorship and reproduction rates when combined with the trace metal contamination presented in the following water chemistry section and should be monitored to ensure sustained aquatic health across the basin.

Water Chemistry

This study found total concentrations of copper and zinc in river waters at Prentiss, Needmore and Cartoogechaye that exceeded guideline values for biotic effects during two separate storm events in 2010. Concentrations appear to be discharge dependent and increase in concentration during larger events with a steep increase observed in the number of samples exceeding aquatic life thresholds from Storm #1 to Storm #2. Both storms sampled in this study were well below the two-year recurrence interval and represent small storms on a historical scale.

Nine other storm events reached similar levels of Storm #1 during the 2010 water year and twelve events occurred which were larger than Storm #1. Only three other events occurred across the 2010 water year that exhibited discharges greater than Storm #2. All four of these events measured just above 5 cm of rain in local USGS raingages. According to these data, mussels may be subjected to increased copper concentrations several times a year relating to increased discharges during storm events.

During the 2010 water year, the peaks for these sites were 45.3 m^3/s at Cartoogechaye Creek, 94 m^3/s at Prentiss and 291.5 m^3/s at Needmore, which are all very near the 2-year recurrence intervals of these sites (Table 3). The back to back hurricanes of 2004 which coincide with the beginning of the most recent large declines in the elktoe mussel populations produced annual peak discharges of 182.3 m^3/s at Cartoogechaye Creek, 317 m^3/s at Prentiss and 591.5 m^3/s at Needmore, which are all close to the 50 year event estimations presented in Table 3. Findings of increased trace metal contamination correlated to increases in discharge, and increasing further from the smaller Storm event #1 to the moderate Storm event #2 raise serious questions to what may be occurring during even larger events. The storms analyzed during this study are occurring at multi-annual intervals and show trace metal contamination above probable effect thresholds.

Comparison of filtered and unfiltered water, obtained from the Isco samplers, shows that the filtered (dissolved) concentrations for copper and zinc are similar to the unfiltered (total) concentrations within the water. In fact, for several samples, the dissolved concentration exceeds the total concentration, a trend that cannot theoretically occur. Such observations have been observed in other studies (Horowitz 1996, Unruh

2009), and are often attributed to (1) variances in concentration within the water sampled, (2) measurement errors associated with the filtration process (Horowitz 1996), (3) desorption of trace metals from the sediments within the Isco samples between the time of collection and time of filtration, (4) phase partitioning in which the majority of trace elements are associated with the colloidal and/or dissolved load and/or (5) analytical errors incurred during the analysis. It is not entirely clear why the dissolved concentrations exceeded the total recoverable concentrations for copper and zinc in this study.

Differences observed between trace element concentrations within porewaters and the river water, collected at different times for different studies suggest that the differences observed between the filtered and unfiltered samples may partly reflect the influence of colloidal particles. The high sorption ability of sediments in the colloidal phase is demonstrated by the large difference in samples collected through 0.20 µm and 0.45 µm filters. This fraction is known to accumulate high levels of trace metals (Miller and Orbock Miller 2007) and is still within the 0.40 µm particle size known to be available to mussels through filter feeding (Strayer 2008).

Factors such as the pH, Eh, contaminated fine particles and presence of sulfide minerals in the bedrock the Upper Little Tennessee River basin lead to the fact that trace metals should be associated mostly with suspended particles. This particulate load can be expected to increase with increased surface flow and disturbance of the bedrock, but is not expected to shift in the dissolved phase. pH levels do not suggest acidity at high enough levels to allow a particulate to dissolved phase shift to occur, although only limited historical pH data is available for larger storm events.

The porewater analysis was carried out as part of a study conducted by the USGS and funded by the US Fish and Wildlife Service. The dissolved phase for this porewater study was operationally defined as 0.20 µm. All waters sampled during porewater analysis were collected through 0.20 µm filters. In contrast, the water column samples collected during this study were filtered through a 0.45 µm filter, the historically used size to define the break between the particle and dissolved phase. Recent studies have shown that significant quantities of trace metals may be associated with colloidal particles that range between 0.1 and 0.45 µm in size (Strayer 2008). In light of the above data, a strong association between trace metals and colloids may explain (1) the differences in concentration between the storm water samples and the porewaters, (2) the high percentage of trace metals associated with the dissolved phase in this study, and (3) dissolved concentrations that exceed total concentrations in some samples.

Sampling time could also have played a large role in the observed differences in concentration between porewater and storm water samples. All porewaters were collected during baseflow, rather than storm events, and during the winter months. Changes in the concentration of these elements certainly occur during fluctuations in discharge, as seen from the storm samples in this project. Moreover, the porewater samples were all collected from August to January, leaving out influence from warmer summer months and the application of copper rich fertilizers and pesticides in the spring.

Several of the porewater samples collected show pH levels in the 5-6 range. With pH at these levels, dissolved concentrations and the mobility of trace elements in the system can increase dramatically, and the mussels can experience heightened stress due to their need to retain a hard protective calcium shell in these highly acidic conditions.

The mussel's ability to pass harmful elements on to their shells also may be reduced. Although high elevation streams tend to have a lower pH, at or below 5.5 (Flum and Nodvin 1985), fish and amphibian populations need to have pH levels above 5.5 in order to survive and reproduce (Borden and Behrooz 2008). Although the average levels of stream pH are not shown at levels detrimental to fish or directly toxic to unionid mussels, the low buffering capacity of these streams makes the waters very vulnerable to chronic acid deposition and increasing stream acidity may result in the loss of aquatic species richness and diversity (NCDENR 1997).

Trace Metal Accumulation in Elktoe Mussels

Accumulation of trace elements in elktoe mussels can be influenced by changes in water chemistry, an individual's location in the river basin, metabolic rate of the individual and the mussel's ability to transfer these elements from soft tissues into their shell (Strayer 2008). Local water chemistry can greatly influence the uptake of trace elements in mussels, including their ability to metabolize otherwise harmful elements (Wang 1995). pH of the local water can change an individual's ability to metabolize elements such as copper and zinc, leading to an influence on the organism's ability to transfer metals from soft tissues, where these elements can be highly detrimental to the mussel, to the shell material where harmful exposure may be reduced.

The high elevation drainages of the Tuckasegee and Little Tennessee Rivers have been shown to exhibit low pH (<5.5) which could lead to an inability of the mussels to deal with concentrations of copper and zinc that exist during storm events. Multi-year sampling of pH across drainages connected with the Great Smoky Mountains by

NCDENR and The National Biological Service along with several of the porewater samples taken during periods of increased discharge in this project show pH levels decreasing below the 5.5 range known to exhibit detrimental effects on biota (Borden and Behrooz 2008). Although limited pH data were collected during this project, and no water quality parameters were collected on the Tuckasegee for comparison, previously collected data show that the Little Tennessee River itself has some of the lowest monitored pH levels. In fact, sites monitored at Prentiss and below Lake Emory exhibit pH levels that drop below 5.5 during storm events and summer months (NCDENR 1997).

pH may be an important factor governing copper and zinc exposure to the elktoe mussel. Once pH drops below 5.5, as seen during porewater collection in this project, the mussels would struggle to metabolize harmful trace metals which they are exposed to (Wang 1995). This can lead to a dangerous combination of pH dropping in the system at the exact time trace element concentrations are increasing due to high water events during storms. Additionally, data from Lake Emory shows that metals are primarily associated with silt and clay sized-particles. The transport of these particles was likely enhanced significantly during the large flood events of 2004. In addition, it is likely that many of the fines deposited during the waning stages of the 2004 events have winnowed (washed) out and are no longer traceable in the Upper Little Tennessee River. This winnowing effect is supported by grain-size data that show bed sediment along the Little Tennessee River typically consisting of < 5 % silt and clay-sized particles (Miller, personal communication 2010). The temporary remobilization and transport of fine-particles could have created an exposure window of highly toxic trace elements to the elktoe mussels during sediment remobilization.

The shell data analyzed during this project show that higher concentrations of copper, zinc and lead exist in shells sampled from the Tuckasegee River, not the Little Tennessee River where population declines have been noted. On the surface, this appears to show that metals are not a significant stressor. Shells from thriving elktoe mussel population were collected from the Tuckasegee River as a control comparison to shells collected in declining populations of the Little Tennessee River. However, if these mussels are truly metabolizing harmful metals into the shell and avoiding some exposure to the soft tissues, just the opposite could be true. Studies have also shown that concentrations found in shell material of freshwater mussels are often the smallest amounts of accumulation when separated out and compared with the soft tissues of mussel gills, mantle, viscera, adductor muscle and foot (Gundacker 2000; Inza 1997). In order to get a better understanding of these processes, further sampling of soft tissue concentrations would need to be analyzed in elktoe mussels from both the Upper Little Tennessee and Tuckasegee Rivers.

Unfortunately, no current toxicity standard for trace metals (including copper) exists for mussel shells. Therefore these observations must be compared with background concentrations of local rocks and soils to obtain an understanding of how these concentrations compare to natural levels commonly found in the environment. Concentrations of trace metals in the shell material can also be compared to recently analyzed water column, porewater and sediment concentrations to produce an understanding of where the mussels are accumulating the potentially harmful trace metal concentrations from.

Copper concentrations in the mussel shells were found to be greater than overlying water and porewater and less than local sediments. These levels could have easily been derived over time through repeated exposure from copper concentrations seen in water grab samples analyzed during this project and/or through direct exposure from more highly contaminated sediments. Copper levels in local sediments in which these mussels live and feed are well above the concentrations observed in shells, however analysis of water grab samples also suggest that these levels of copper are readily available during storm events and not only a long-term bioaccumulation threat to the elktoe mussels. Combined with increasing copper concentrations during storm events, already elevated concentrations of trace metals, such as copper, in the sediments could quickly become deadly to these organisms as well as other surrounding aquatic biota. In addition, these elktoe shells were collected freshly dead to moribund, so we cannot say these particular individuals were unharmed by the copper concentrations observed.

Porewater

During this study, porewater sampling of overlying water, 0-3 cm sediments, and 7-10 cm sediments was only funded for ammonia and copper trace metals due to monitoring costs and the higher historical relationship between mussel shells and copper as a trace metal contaminant. Porewater samples collected along the lower reaches of this study, where prominent elktoe mussel habitat exist, show extremely low levels of copper contamination compared to sediment, mussel shell and water grab sample concentrations. Looking at this porewater data alone, it appears that copper concentrations are such that contamination is not a problem. Some issues with relying solely on these data to determine levels of copper in the Upper Little Tennessee River basin include the limited seasonal variability during which these samples were collected, the filter size used during sampling procedures and possible localized and stream-wide variability.

Bed sediment concentrations of several trace metals (chromium, copper, nickel, lead and zinc) exceeded probable effects thresholds along sections of the Little Tennessee River basin included in this study (Miller 2010). These data are consistent with water chemistry results from this study and raise further caution to the possible threats to aquatic life in the basin from trace metal contamination. Threats from sediment contamination relate to water quality and aquatic life thresholds through trace metal contamination, direct contact between sediments and aquatic life, filter feeding in the water column and the ability of these trace elements to change phase during environmental fluctuations.

Some studies have shown that filter feeders, such as the elktoe mussel, can accumulate metals from particles up to 0.40 µm in size (Bronmark and Malmqvist 1982, Vanderploeg 1995). It follows, then, from concentrations observed for both the filtered and unfiltered water samples that copper and zinc may be a significant stressor. These elements are seen at increased levels above the aquatic life threshold and should be taken into consideration as a factor in the demise of elktoe mussel populations across the Little Tennessee River. Although a significant question is raised by higher concentrations of copper and zinc in the dissolved phase than the total phase, the total recoverable concentrations are still above water quality thresholds and warrant further investigation into metal contamination during storm events. Although copper samples are not easily contaminated, the high dissolved concentrations seen in these samples make them suspect and should be considered with an air of caution. The total recoverable concentrations can be used with a higher degree of certainty, and were not exposed to the filtering process where sample contamination may have occurred.

Local water chemistry determines whether these particles are in suspended, colloidal, or dissolved phase and surface-water and porewater chemistry can change seasonally and during environmental fluctuations, such as storms and large rain events. Therefore, the fraction of these harmful trace metal concentrations which can be considered as bioavailable may change through time. Trace elements were found during this study at levels of probable effect concentrations in the sediments, beyond the NC standards for aquatic life for copper and zinc in the water column and at elevated concentrations in mussel shells. These elements also displayed an ability to fluctuate from ambient to harmful concentrations during changes in discharges as noted in the results for trace metal concentrations of copper during Storms #1 and #2, as well as, zinc and nickel during Storm #2.

CONCLUSION

Observations in the Upper Little Tennessee River show that several trace metals including copper, chromium, lead, nickel and zinc are present in the sediments of both Lake Emory and the river channel and floodplain of the Upper Little Tennessee River below Lake Emory at concentrations above probable effect thresholds (Miller 2010). The sediments sampled below the Lake Emory dam include habitat of the elktoe mussel and reaches where large declines have recently been determined. Findings in freshly dead and moribund elktoe mussel shells from March 2010 show diluted amounts of these trace metal contaminants compared to sediment concentrations. Levels of trace metals contamination observed in the shells are elevated above water column and porewater concentrations, but less than the concentrations levels of Upper Little Tennessee River sediments. Furthermore, water grab samples taken during storm events along the Upper Little Tennessee River show levels of copper and zinc elevated above the aquatic life thresholds for NC waters. These samples were taken during rain events in the basin and demonstrate fluctuations of trace metal concentrations with changes in discharge.

Trace metal contamination was observed to be highest in the water grab samples, present in mussel shell samples and non-existent in porewater samples. Differences seen between porewater, mussel shell and water grab samples can be attributed to several factors including the ability of metals to vary widely in water depending on stream-flow conditions, ground- and surface water flow and temporal variations in loading from various sources. The water grab samples analyzed during this project represent samples taken at high stream, surface and possibly ground water flows, while the porewater samples were collected during ambient low-water discharges. Also, porewater samples were collected through 0.20 μm filtration, while stream-water grab samples were collected through 0.45 μm filtration.

The observations that trace metals are present at probable effect levels in the sediments and at levels above aquatic life thresholds in the water grab samples strongly suggest that these factors could lead to decreases in elktoe mussel survival rates. Large storms, such as the back to back hurricanes of 2004 present in the basin just prior to large observed declines in elktoe mussel populations could lead to drastic changes in water and porewater chemistry and greatly affect particulate phase partitioning and the bioavailability of these elements.

Historical pH ranges in the Upper Little Tennessee River basin demonstrate a tendency for large decreases in pH during high water events (NCDENR 2004). Coupled with trace metal concentrations above aquatic life threshold limits, a decreasing pH may lead to an inability of the mussels in the Little Tennessee River to cope with elevated levels of copper, lead and zinc contamination. Although concentration levels are greater in mussel shells analyzed from the Tuckasegee River, differences in pH between these two rivers may determine the mussel's ability to cope with trace metal contamination.

Water quality data collected in upstream sites of the basin demonstrate dissolved oxygen and turbidity parameters in excess of aquatic life thresholds. At the downstream data collection site, where elktoe mussel populations were once sustained, dissolved oxygen levels do not appear to be an issue; however, large increases in turbidity during storm events may be combining with other stressors in the basin to contribute to negative results on survivorship of this species. Overall, ambient conditions observed during base flow at all three sites appear to demonstrate a healthy aquatic environment. However, during storm events trace metal concentrations and turbidity values raise caution due to common exceedance of aquatic life thresholds.

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